STUDIES IN *peri*-NAPHTHALENES

A thesis presented for the degree
of Doctor of Philosophy in Chemistry
at the University of Canterbury
Christchurch, New Zealand

by

R.A.
David Leonard

1971

ABSTRACT

1,2,3,4,7,8,9,10-Octahydrodicyclohepta[*de*,*ij*]naphthalene (**17**) and 2,3,6,7,8,9-hexahydro-1*H*-cyclohepta[*gh*]phenalene (**46**) have been prepared via benzsuberone (**22**), the tricyclic ketone 1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**), and the tetracyclic ketones 1-oxo-1,2,3,4,4a,5,6,6a,7,8,9,10-dodecahydrodicyclohepta[*de*,*ij*]naphthalene (**30**) and 1-oxo-2,3,6,7,8,9-hexahydro-1*H*-cyclohepta[*gh*]phenalene (**45**), respectively. 5,6,7,8-Tetrahydrocyclohepta[*fg*]acenaphthene (**57**) was also prepared, by an improved method.

The dicycloheptanaphthalene **17** and the cycloheptaacenaphthene **57**, along with the tricyclic ketone **14** and the carbocyclic benzenes indan (**64**), tetralin (**65**), and benzsuberan (**66**) were reacted with mixtures of fuming nitric acid and acetic anhydride, and the resulting nitro-acetoxy adducts were isolated.

The evidence for the structure of the hydrocarbons, their precursors, and their nitro-acetoxy adducts is discussed, and mechanisms are suggested for their formation.

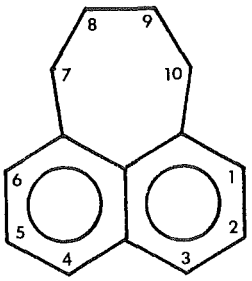
CONTENTS

SYNTHETIC SCHEMES

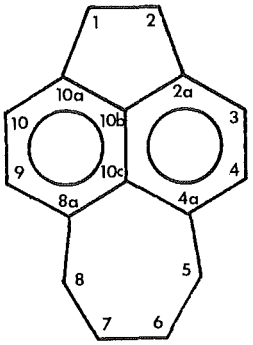
NOMENCLATURE

The numbering systems of the carbon skeletons of the polycyclic systems encountered in this work are shown in figure 1. The systematic names of the unsubstituted hydrocarbons are respectively 7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene (I), 5,6,7,8-tetrahydrocyclohepta[*fg*]acenaphthene (II), 2,3,6,7,8,9-hexahydrocyclohepta[*gh*]-1-*H*-phenalene (III), and 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*]naphthalene (IV). These names were derived using I.U.P.A.C. rules[1].

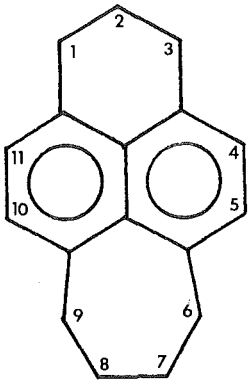
In the cases of the phenalene and acenaphthene the trivial but recognised names (rules 21.2 and 23.1) were retained for brevity. Strictly systematically, the acenaphthene is named 1,2,5,6,7,8-hexahydrocyclohepta[*de*]cyclopenta[*ij*]naphthalene. The trivial names for the hydrocarbons are respectively pleiadane, acepleiadane, peripleiadane, and dipleiadane. While these names are concise, they are misleading to readers who are unfamiliar with *peri*-cyclic naphthalenes. This is mainly because pleiadene is the name commonly given to the tetracyclic compound with a third six-membered aromatic ring fused across the 8,9 bond of pleiadane[2] (see figure 8).



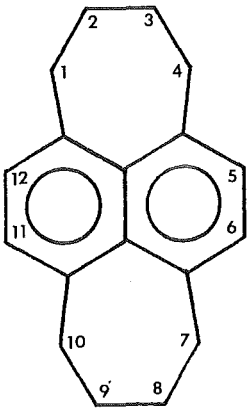
I



II



III



IV

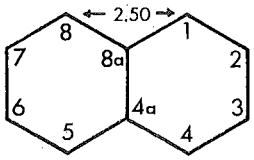
FIGURE I

INTRODUCTION

The *peri* positions of the naphthalene molecule are the 1-, 4-, 5- and 8-positions. The 1- and 8-positions and the 4- and 5-positions are said to be *peri* to each other, whereas all other adjacent positional relationships are *ortho*.

Structural Evidence for *peri*-Interaction

From the geometry of the naphthalene molecule (figure 2) it can be seen that the hydrogens *peri* to each other are in closer proximity than those *ortho* to each other. Even when the *peri*-substituents are hydrogens, X-ray diffraction data[3] suggests that the naphthalene molecule undergoes in-plane distortion to reduce the *peri*-hydrogen interaction. Hence the angle formed by carbons 1, 8a, and 8 is 121° 31' rather than the classical 120° (see figure 2). 1,8-Dimethylnaphthalene would have a large *peri*-interaction compared with naphthalene and hence the angular distortions should be exaggerated. Although the X-ray diffraction study of this molecule was started some years ago[4], the detailed structural analysis has not yet been published. However, Jameson and Penfold, of this department, have determined the



121.5	<1 8a 8	126.8
119.2	<1 8a 4a	114.0
120.3	<7 8 8a	119.4
120.5	<6 7 8	121.4
	<8 8a 4a	119.2
	<4 4a 5	117.4

FIGURE 2

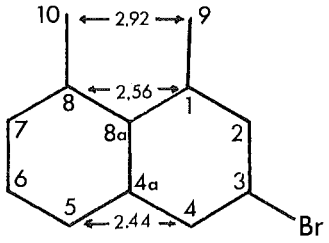


FIGURE 3

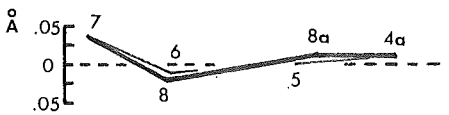


FIGURE 4

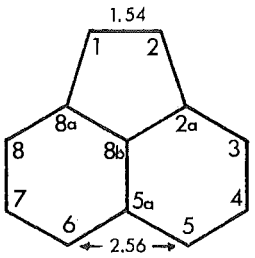


FIGURE 5

crystal structure of 3-bromo-1,8-dimethylnaphthalene[5]. They found that the overcrowding of the *peri*-methyl groups causes the molecule to undergo considerable in-plane distortion (see figure 3). The methyl groups are pushed apart by approximately 0.42 angstroms. This causes the $C-CH_3$ bonds to bend outwards by 4° each, and increases the angle 1 8a 8 by 5.3° relative to naphthalene, as well as the non-bonded distance between carbons 1 and 8 by 0.06 angstroms. In concert with these increases the angle 4 4a 5 is decreased by 4.1° and the non-bonded distance of carbons 4 and 5 is shortened by 0.06 angstroms. Besides the large in-plane distortion the molecule was found to undergo small but definite out-of-plane distortion. Only one atom (C-10) exhibits a significant departure (0.097 angstroms) from the mean plane of the naphthalene skeleton, but ring A is buckled such that some carbons are as much as 0.03 angstroms out of the mean plane of the naphthalene skeleton (figure 4). Ring B undergoes very little out-of-plane distortion but on the other hand has larger in-plane distortion than ring A. This was attributed to ring B containing the heavy bromine atom. It was further suggested that similar distortions to those observed for 3-bromo-1,8-dimethylnaphthalene occur in 4,5-dimethyl-1- and 2-naphthoic acids. These acids have a slightly (but measurably) lower

dissociation constant than their corresponding naphthoic acids[6]. The decrease in the acidity of the 4,5-dimethyl naphthoic acids was said to be caused by the mesomeric stabilisation of the anion being reduced by the buckling of the naphthalene skeleton. The significance of this complementary observation is that the buckling of the naphthalene skeleton would appear to be an intrinsic property of the molecule, and not a configuration forced upon it by crystal lattice interactions.

Similar buckling of the naphthalene skeleton has also been observed for 1,4,5,8-tetra-chloronaphthalene[7]. The chlorine atoms alternate with respect to those atoms

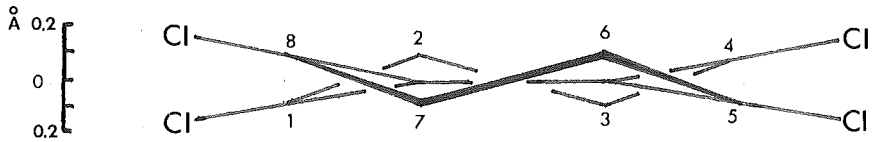


FIGURE 6

both *peri* and *para* to them so that they are 0.18 angstroms above or below the mean plane of the naphthalene skeleton. This results in the naphthalene nucleus forming a twin non-eclipsed chair-like conformation (figure 6).

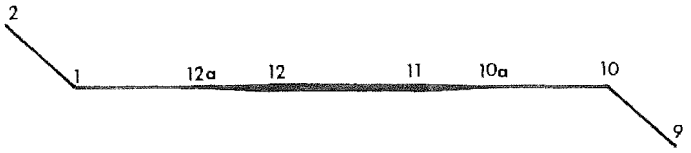
It is interesting to note that the structural analysis of 1,5 dinitronaphthalene[8] shows it to have in-plane distortion of the same order as 3-bromo-1,8-dimethylnaphthalene. However, the naphthalene ring does not depart from planarity. The *peri*-interactions are relieved by the nitro groups being twisted 49° out of the plane of the molecule as well as by in-plane distortions. 1,8-Dinitronaphthalene also undergoes these types of distortion, and although the distortions are very large (the angle 1 8a 8 is 130°) they alone cannot relieve the severe crowding of two nitro groups *peri*- to each other and the naphthalene nucleus is also buckled[9].

Acenaphthene (figure 5) also exhibits in-plane distortion[10]. The length of the C-1, C-2 bond is 1.54 angstroms, or a normal carbon-carbon single bond length. The lengths of bonds in the aromatic nucleus are similar to those for naphthalene. In order to accommodate these normal bond lengths the molecule exhibits marked angular distortion such that the angle 8a 8b 2a is 112.4° and the angle 5 5a 6 is 128.4°. Consequently C-5 and C-6 are

splayed apart such that their non-bonded distance is 0.06 angstroms greater than the corresponding (C-4, C-5) distance in naphthalene. Here we have an example of *peri*-substituents causing in-plane distortions opposite to those found in 3-bromo-1,8-dimethylnaphthalene.

Proposal for the synthesis of 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*]naphthalene

The nuclear out-of-plane distortions found in 3-bromo-1,8-dimethylnaphthalene led to the proposal of the synthesis of 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*] naphthalene (IV). Inspection of a Dreiding model of this molecule indicated that the molecule could exist in a "chair" or "boat" conformation with respect to the orientation of the aliphatic bridge carbons -2, -3, and -8, -9, in which case the naphthalene nucleus would be planar; or in a puckered conformation, in which case the naphthalene skeleton would be buckled (figure 7). These are the extreme cases. A conformation intermediate to these is, of course, possible. It is possible for the "chair" and "boat" conformers to interchange, although manipulation of the model suggested that the barrier to interconversion would be quite high. Interconversion of the "chair" and "boat" forms would occur with greatest ease when the molecule assumes an intermediate puckered conformation. The formation of the puckered conformer would be encouraged by the reduction of interaction



"CHAIR"

"BOAT"

PUCKERED

FIGURE 7

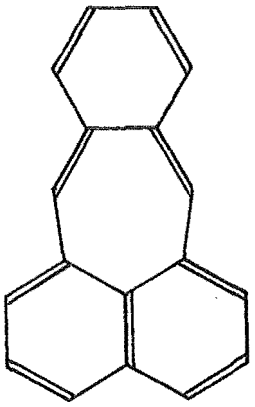
of the *peri*-methylene groups as they move out of plane in opposite directions, and by the *peri*-carbons *para* to each other moving in sympathy in order to form a chair-type conformation. This is similar to the conformation assumed by 1,4,5,8-tetrachloronaphthalene, which was discussed previously. The buckling of the naphthalene skeleton is not likely to be as large as that for the tetrachloronaphthalene, as the *peri*-interaction of two chlorine atoms would be larger than that of two methylene groups. However, the degree of buckling should be larger than that for 3-bromo-1,8-dimethylnaphthalene. In the latter the strain caused by the interaction of the two methyl groups is mitigated to some extent by the compression of the *peri*-carbons at the opposite end of the molecule (the non-bonded distance of carbons -4 and -5 is 2.44 angstroms and the angle 4 4a 5 is 117.4° cf. 2.50 angstroms and 121.5° in naphthalene). In the dicycloheptanaphthalene the same type of interactions would occur at both pairs of *peri*-positions and hence some other form of steric relief, presumably nuclear buckling, would be required.

The proposed dicycloheptanaphthalene contains hydrogens which appeared promising for study by nuclear magnetic resonance (n.m.r.) spectroscopy. The protons of the methylene groups α to the naphthalene nucleus are in distinctly different environments in any of the three

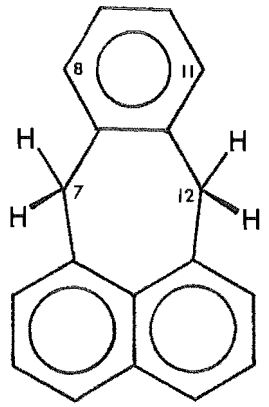
extreme conformers. One proton tends to lie in the plane of the naphthalene nucleus and the other between 45 and 90° out-of-plane. The protons of the β-methylenes are less distinctive, but it was thought that they may have different chemical shifts owing to one of them pointing towards the anisotropic cone of the naphthalene nucleus and the other away.

N.m.r. studies of seven-membered *peri*-cyclic naphthalenes

7,12-Dihydropleiadenes, compounds closely related in structure to the proposed dicycloheptanaphthalene (see figure 8), have recently been studied extensively by Lansbury and co-workers[11]. By studying the n.m.r. characteristics of the protons on the hinge carbons (carbons -7 and -12) they were able to calculate the free energy barriers for ring inversion of various substituted 7,12-dihydropleiadenes. The dihydropleiadene system is particularly suitable for ring inversion studies because the hinge-carbon protons are decidedly axial or equatorial and their protons have different chemical shifts and well-defined coupling constants. Using variable temperature n.m.r. spectroscopy it was found that the axial and equatorial protons gave a well-separated pair of doublets when the rate of inversion was slow, and that these lines coalesced to a single signal when inversion was fast. Thus

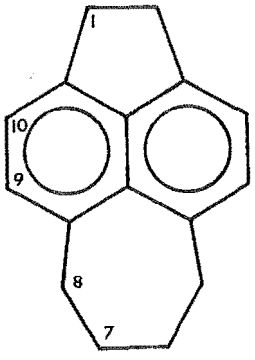


PLEIADENE



7,12-DIHYDROPLEIADENE

FIGURE 8



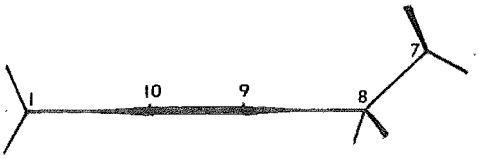


FIGURE 9

Lansbury *et al* were able to calculate the rate of inversion at the coalescence temperature by using an expression involving the difference in chemical shift of the axial and equatorial protons before coalescence[12]. From the rate equation the rate constant was obtained and this was used to calculate the free energy of activation of inversion at the coalescence temperature. They found that where the free energy barrier to inversion was suitably high (in excess of 20 kcal/mole) the individual conformers were isolable, and that with lower barriers (between 10 and 20 kcal/mole) the conformers could be detected by n.m.r. spectroscopy. The unsubstituted 7,12-dihydropleiadene was an example of the latter.

When the pleiadene was substituted with 8-methyl and 8,11-dimethyl substituents the free energy barrier to inversion was found to increase linearly. This was said to be indicative of a planar transition state as the 8- and 11-substituents interact with the hinge protons, and have an inhibitory "buttressing effect" upon ring inversion[10]. The methyl groups substituted *ortho* to the inverting methylene carbons cause more steric compression in the transition state (when the angles in the seven-membered ring spread out) than in the ground state. The dicycloheptanaphthalene is unlikely to have a planar transition state for the inversion of its rings. In order for one

of the seven-membered rings to be planar it must exert a large expanding strain on the *peri*-carbons on which it is substituted. In doing so it transmits across the ring a compressive stress on the opposite *peri*-carbons. These, however, are already under an expanding strain from the other seven-membered ring, and it is unlikely that these carbons would undergo any sympathetic in-plane distortion. A planar seven-membered ring is more strained in the dicycloheptanaphthalene because the C-2, C-3 bond is aliphatic whereas the corresponding C-7a, C-11a bond in dihydropleiadene is a shorter aromatic bond. This causes a greater splaying of the hinge carbons and the internal angles have more difficulty in accommodating among them the required 900° for a planar seven-membered ring. Further, the C-2, C-3 bridge of the dicycloheptanaphthalene is more flexible than the highly rigid C-7a, C-11a bridge in the dihydropleiadene. This allows for twisting about this bond and this results in a transition state of a puckered-type conformation being formed. It is our contention that this is the more energetically favoured mode of inversion.

A molecule which promised to be of interest for comparative studies with the dicycloheptanaphthalene was 5,6,7,8-tetrahydrocyclohepta[*fg*]acenaphthene (figure 9). Apart from the C-6, C-7 bridge the carbon skeleton of this

molecule should be completely planar, as all distortion from *peri*-methylene interaction should be accommodated by in-plane distortion. This is because the compression exerted on the *peri*-carbons -2a and -10a in order that the acenaphthene bridge might be formed results in the splaying of the opposite *peri*-carbons by a distance of the same order as that required for those carbons to accommodate two non-bonded methylene groups (see figures 3 and 5). The seven-membered ring of the cyclohepta-acenaphthene should have a higher barrier to inversion than the dicycloheptanaphthalene because the opposing five-membered ring makes the naphthalene nucleus very rigid and inversion of the seven-membered ring by twisting about the C-6, C-7 bridge bond is more inhibited.

Structure elucidation of carbocyclic compounds using fluorine magnetic resonance spectroscopy

It was suggested[13] that the proton-proton relationships in the alicyclic rings of 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*]naphthalene would be shown more explicitly if a fluorine atom was substituted into one of those rings. By this means it was hoped to determine the conformation of the alicyclic rings.

When fluorine is substituted in an organic molecule it may act as a "stereospecific" probe. This is because certain ^{19}F n.m.r. parameters are extremely sensitive

to the steric environment of the fluorine substituent under investigation[14]. For example, the chemical shift separation (at low temperatures) between axial and equatorial proton resonances (δae) of cyclohexane is 0.47 p.p.m.[15]. The separation of the corresponding fluorine resonances in perfluorocyclohexane is 18.2 p.p.m.[16], or about forty times greater. In cyclohexylfluoride the δae value for H-1 resonances is only 0.46 p.p.m., whereas the δae value for the F_1 resonances is 20.5 p.p.m.[17]. Thus the fluorine chemical shift is approximately 45 times more sensitive to the steric environment than is the shift of the proton which is attached to the same carbon. The ^{19}F-^{1}H couplings also show a greater sensitivity to steric environment than corresponding ^{1}H-^{1}H couplings, owing to their magnitude being several times greater.[14] Vicinal couplings appear to have a dihedral angular dependence similar to that for ^{1}H-^{1}H vicinal couplings[14]. Hence, not only may the orientation of the fluorine atom be determined from its chemical shift, but also the relative orientation of the adjacent carbon atoms may be inferred. A further advantage in having a dual magnetic nuclear system is that the ^{19}F-^{1}H couplings show on both ^{19}F n.m.r. and ^{1}H n.m.r. spectra, and by comparing these spectra the assignment of frequencies to protons is simplified.

It would be hoped that the substitution of a

fluorine atom in an alicyclic ring in order to elucidate its conformation would not at the same time alter the conformation of that ring. Considering the small size of the fluorine atom this assumption seems reasonable, and while this appears to be the general case some examples of esterified pentapyranosyl fluorides have been cited[18] in which a powerful "anomeric effect"[19] of the fluorine substituent has been sufficiently dominant to exert control over the conformation of the molecules.

Fluorination of carbons α to the naphthalene nucleus

In order to elucidate the conformation of the alicyclic rings of the dicycloheptanaphthalene by ^{19}F n.m.r. studies, we required a method of selectively inserting a fluorine atom into one of the rings. The carbon α to the aromatic nucleus is the more reactive of the aliphatic carbons, and this appeared to be the obvious site for fluorine substitution. The literature contains many instances of carbon-fluorine bond formation, but none in which the site of formation is α to both an aromatic ring and a saturated carbon. The carbon-fluorine bond is very stable (bond energy c.a. 107-121 kcals/mole, cf. 81 kcal/mole for C-Cl) but its formation is often difficult. Direct fluorination with elemental fluorine is difficult to control because the energy released in the

formation of C-F and H-F bonds is greater than the energy required to break other bonds such as C-C, C-H, and C-Cl. This problem may be overcome by using inorganic fluorine carriers such as silver (II) fluoride, or by passing diluted gaseous mixtures of fluorine through cold solutions of an organic compound in freon.

The most common mode of formation of a C-F bond is by nucleophilic substitution by a fluoride ion. Even this is not a particularly well-favoured reaction. Although the resultant C-F bond is very strong, the replacement of the incumbent group is inhibited by the low polarizability and consequent weak nucleophilicity of the fluoride ion. Ionic substitution reactions must be carried out under anhydrous conditions because the fluoride ion in aqueous solutions has a tightly bound shell of water molecules about it which further reduces its nucleophilic character. A comprehensive treatment of C-F bond formation by nucleophilic substitution has been written recently by Sheppard and Sharts[20]. Antimony tri- and pentafluorides were early (and in some cases efficient) fluorinating agents. Antimony trifluoride has a reactivity comparable to anhydrous hydrogen fluoride, but is unreactive towards double bonds. It has been known to replace chloride at benzylic positions[21] but the site of substitution was activated by additional chlorine atoms, and the reaction required heating in order

to proceed. Silver fluoride has been used to fluorinate some relatively complex molecules[14,22], but has the disadvantages of tending to cause the elimination of hydrogen halide (in the substrate) and of being an expensive reagent. In many cases it has been superseded by mercury (II) fluoride, which in turn has been superseded by potassium fluoride. Potassium fluoride has been used with considerable success in the replacement of halides when the reaction has proceeded in polar aprotic solvents at elevated temperatures. Benzylic[23] and naphthyl methyl bromides[24] have been successfully fluorinated in N-methylpyrrolidone.

A recent advancement in organic fluorination techniques was the discovery that sulphur tetrafluoride will replace the oxygen of a carbonyl group with two fluorine atoms[25]. Reactions may be catalysed by hydrogen fluoride or boron trifluoride, or conversely controlled by dilution using solvents such as methylene chloride. The reaction is carried out under autogenous pressure in a bomb, and the preferred temperature for ketones appears to be 50-100°, or higher if the carbonyl group is hindered or deactivated.

Spectral evidence for *peri*-interaction

Balasubramaniyan[26] has collected a large number

of instances where effects on ultraviolet, infrared, and n.m.r. spectra have been attributed to *peri*-interaction.

The ultraviolet absorption spectrum of naphthalene consists of three absorption bands with λ_{max} at 220 (ε = 1,000), 275 (ε = 500), and 312 nm (ε = 20 m^2 mol^{-1}). With the introduction of substituents, the band positions and intensities are modified to a degree dependent upon the substituent. The spectrum of the substituted naphthalene depends on whether or not the substituent conjugates with the aromatic nucleus and on the presence or absence of steric interaction. The comparison of a number of mono-substituted naphthalenes has shown that with α-substitution the 275 nm band is bathochromically shifted and superimposed on the weaker 312 nm band, and with β-substitution the 275 nm band is unaffected but the 312 nm band is shifted to longer wavelengths. This effect has been attributed to the greater conjugating power of the α-positions compared to the β-positions[27], but there is also evidence, gained from the study of polymethylnaphthalenes, that steric interaction may contribute to this shift[28,29]. It has also been suggested, from the study of *peri*-halo and -sulphur derivatives of naphthalene, that bathochromic shifts in the 275 nm and 312 nm bands of naphthalene are caused by interpenetration and consequential conjugation of the π-electron clouds of the *peri*-substituents[30]. Further studies

of the effect were carried out by examining the absorption spectra of 1-naphthylthioglycollic acids[31]. For 8-substituents it was found that the magnitude of the shift could be directly related to the number of non-bonded electrons on the substituent. Unfortunately an 8-methyl substituted compound was not studied, but the 8-carboxylic acid derivative was, and this had the same λ_{max} as the unsubstituted 1-naphthylthioglycollic acid. In these cases it would appear that the *peri*-effect is due to a conjugative rather than a steric interaction.

Infrared spectroscopy has indicated anomolous vibrational behaviour of substituted naphthalenes which may be interpreted as being caused by *peri*-interaction. 1,8-Disubstituted naphthalenes show two strong bands in the region of hydrogen bending vibrations (740-850 cm^{-1})[32]. This is surprising, because as 1,8-disubstituted naphthalenes have two sets of three adjacent hydrogens only one vibration in this region would be expected[33]. Topsom *et al* have suggested that the extra band might be due to the symmetry of these compounds. However, if there is nuclear distortion the two sets of protons will no longer be equivalent, and this could be the origin of the extra band. *Peri*-interactions are more readily seen in the changes in frequencies of *peri*-substituents. For example, the stretching frequency of aromatic carbonyl functions

normally occurs around 1690 cm^{-1}. For *peri*-substituted compounds it is found to occur at higher frequencies[34], because owing to steric interaction the carbonyl group is forced out-of-plane from the aromatic nucleus and conjugation is inhibited.

Nuclear magnetic resonance spectroscopy has revealed many instances of *peri*-interactions manifested by the chemical shifts of both aromatic and substituent protons. It is difficult to determine the origin of the shifts, for these may be the result of electronic, steric, or anisotropic effects of the substituent. However, in some cases it is apparent that one of these effects is dominant. The α-protons are deshielded even in naphthalene itself (2.20 τ cf. 2.56 τ for β-protons[35]). When the *peri*-substituent is an electron-withdrawing group the chemical shift of the adjacent *peri*-proton is usually moved further downfield. In naphthalene-1-sulphonic acids this effect is small compared to the displacement of the protons *ortho* and *para* to the substituent. The latter shifts are attributed to the mesomeric withdrawal of electrons from these (*ortho* and *para*) positions[35]. In 1-nitronaphthalene the displacement of the *peri*-proton is large (1.64 τ cf. 2.20 τ for naphthalene) and this is attributed to the anisotropy of the nitro group[36]. However, in 1-nitro-2-methyl naphthalene the chemical shift of the

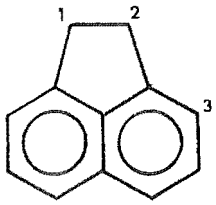
peri-proton is moved upfield to 2.32 τ. This anomoly is thought to be due to a re-orientation of the anisotropic axis of the nitro group owing to the nitro group being pushed out of the aromatic plane by the methyl group and the *peri*-hydrogen[36]. Another effect causing downfield displacement of the *peri*-hydrogen frequency is a type of hydrogen bonding[37]. In 5-acetylacenaphthene and 1-methoxynaphthalene the *peri*-hydrogen and oxygen atoms are closer together than the length of a normal hydrogen bond, and it is this type of interaction which is thought to deshield the aromatic *peri*-protons.

When the substituents in the naphthalene nucleus are electron donating the chemical shifts of the protons are generally moved upfield, but the shift is less for α- than β-protons. When the protons are *peri* to a methyl group, even though they might be *para* to another group, they are shielded less than when *ortho* to a methyl group[38]. The aliphatic protons of α-substituted methyl groups are also deshielded compared with β-protons.

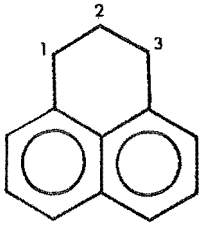
The formation of *peri*-fused carbocyclic naphthalenes

Peri-cyclic naphthalenes incorporating five to eight carbons in the *peri*-cycle are known. The most common type of *peri*-cyclic naphthalene incorporates a six-membered ring (phenalene derivatives) followed by

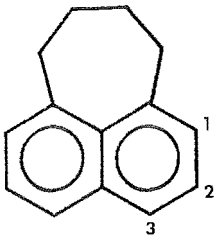
five-membered ring compounds (acenaphthene derivatives), seven-membered ring compounds (homophenalene derivatives), and eight-membered ring compounds.



ACENAPHTHENE



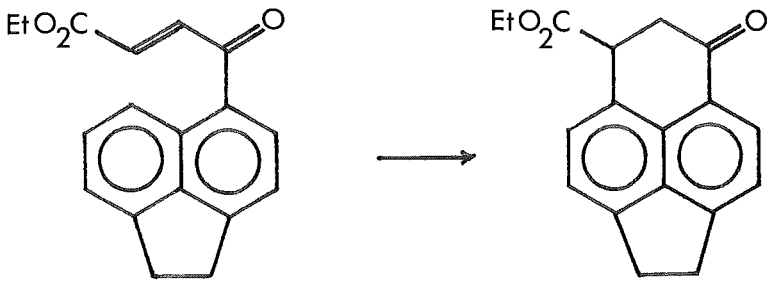
2,3-DIHYDRO-1H-PHENALENE



HOMOPHENALENE (7,8,9,10-TETRAHYDROCYCLOHEPTA-[*DE*]NAPHTHALENE)

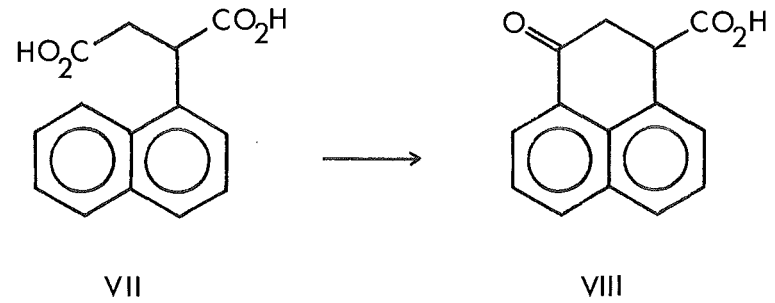
The general mode of formation of carbocyclic *peri*-naphthalenes is by the closure of an α-substituent into the position *peri* to it. Usually the terminal function of the chain which forms the ring is a carboxylic acid or a carboxylic acid derivative. There are also instances of compounds containing unsaturated side-chains undergoing intramolecular addition reactions whereby the naphthalene nucleus adds to the double bond to form a *peri*-cycle. For example, ethyl 4-(5'-acenaphthenyl)-4-oxo-but-2-enoate (V)

will cyclise to give the phenalene derivative VI[39]. In many

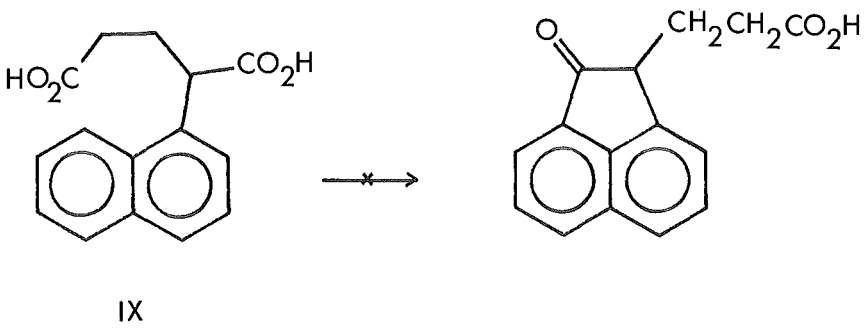


V VI

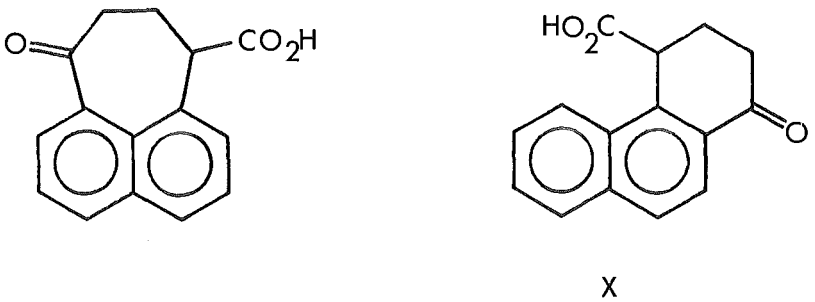
cases there is the possibility of ring closure at more than one position (notably 1,8 and 1,2 closure). There are many factors which may dictate the preference of a chain to close at one position rather than another. The size of the ring to be formed is an important factor. Naphthalenes α-substituted with a four-membered chain (homophenalene precursors) preferentially close into the β-position (to form phenanthrene derivatives) rather than the *peri*-position unless the β-position is already substituted or the *peri*-position is highly activated towards electrophilic attack. Where there is the choice of a five- or six-membered *peri*-cycle, such as in 1-naphthyl succinic acid[40] (VII, figure 10), the phenalene derivative (VIII) rather than the acenaphthene derivative is the favoured product. The relative



VII VIII



IX

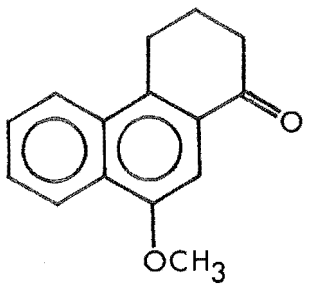


X

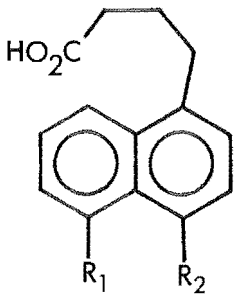
FIGURE 10

favourability of five- and seven-membered *peri*-cycle formation would be shown by α-(1-naphthyl) glutaric acid (IX) were it not for its preferential β-closure to form the phenanthrene derivative X[41].

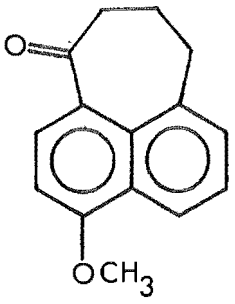
The nature of other substituents in the naphthalene nucleus is an obvious factor affecting the direction of ring closure. The effect of other substituents is particularly noticeable in the formation or attempted formation of homophenalene derivatives. When the acid chloride of 4-(4'-methoxy-1'-naphthalenyl) butanoic acid (XI, R_1 = H, R_2 = OCH_3) was subjected to Friedel-Crafts cyclization the phenanthrenone XII was the reported product. When 4-(5'-methoxy-1'-naphthalenyl) butanoic acid (XI, R_1 = OCH_3, R_2 = H) was reacted under similar conditions the homophenalene derivative was isolated[43]. To form the seven-



XII

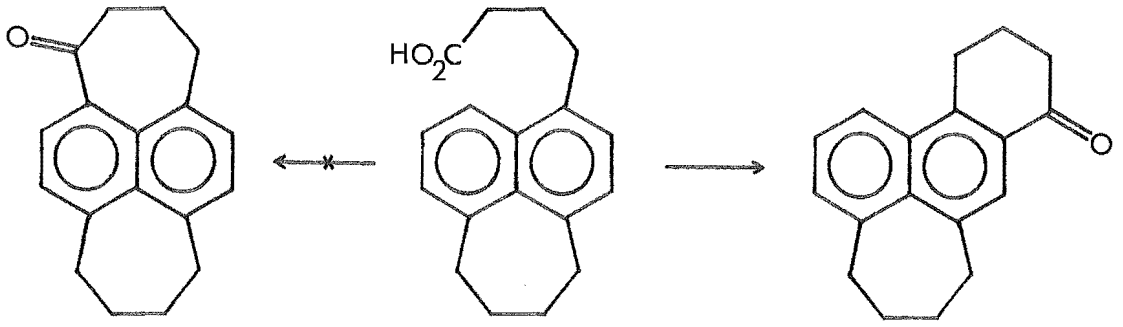


XI



XIII

membered ring the activation of the *peri*-position must be large in order to overcome the normally preferred formation of the six-membered ring. In the cycloheptanaphthalenyl butanoic acid XIV the tetramethylene bridge would activate to a greater extent the position *peri* to the butanoic chain than the position *ortho* to it. However, when it was cyclised under the influence of phosphorus pentoxide and stannic chloride the α,β-fused ring was formed[44]. This



XV XIV

result was unfortunate, because had *peri*-closure occurred, the resulting ketone XV would have been easily reduced to 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*]naphthalene. *Peri*-closure was achieved for the homologous system methyl 4-(5'-acenaphthenyl)-4-oxo-butanoate[39] (**55b** page 72). The factor contributing most to the acenaphthene derivative's

ability to undergo *peri*-cyclization is probably the presence of the keto group α to the aromatic ring. This would deactivate that ring towards further electrophilic substitution. The second ring would also be deactivated, but to a much lesser extent, and off-setting this the *peri*-position would be activated by the ethylene bridge at the other end of the molecule. The 5- and 6-positions of acenaphthene are known to be highly activated towards electrophilic attack[45]. Furthermore, as discussed earlier, the acenaphthene nucleus is better able to accommodate (on steric grounds) a *peri*-fused seven-membered ring than is the cycloheptanaphthalene derivative. In homophenalene preparation via ring closure, the need for activation of the adjacent *peri*-position, or the need for deactivation of the ring bearing the butanoic chain, is removed if this ring is saturated. The tetrahydrobutanoic acid would then have no alternative but to close into the sole aromatic nucleus. This route is also favoured by a decrease in the strain in the seven-membered ring formed, owing to a greater flexibility of the molecule. The more successful preparation of 7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene made use of this principle[46]. Phenalene derivatives have also been prepared by the cyclization of a precursor containing only one aromatic ring. However, unless 2,3,3a,4,5,6-hexahydro-1H-phenalene derivatives themselves are

desired, this synthetic mode has little application, as *peri*-substituted naphthalenylpropanoic acids normally readily undergo *peri*-closure. Further, if a 2,3-dihydro-1-H-phenalene derivative is required, which is often the case, difficulty may be experienced in obtaining the desired isomer. This is because dehydrogenating agents are generally not selective as to which ring they aromatise.

In the cyclization of fully aromatised 3-(1'-naphthalenyl)propanoic acids the position and type of substituent may have significant influence on the position of closure. Obviously, 2'-substituents prohibit 1',2' cyclization regardless of whether or not they activate the 8'-*peri*-position. Electron donating 5'- and 7'-substituents activate the 8'-position, but 6'-substituents activate the 2'-position more than the 8'-position, and 1',2' closure occurs[47]. *Peri*-cyclization of 3-(7'-alkyl-1'-naphthalenyl) propanoic acids occur smoothly except when the alkyl group is tertiary butyl. Owing to the severe steric hindrance of the tertiary butyl group *peri*-closure will occur only under severe conditions, and only after the bulky substituent has been lost.

The condensing agent may have a marked effect on the nature of the product. When 4-(5'-methoxy-1'-naphthalenyl) butanoic acid (XI, $R_1 = OCH_3$, $R_2 = H$) was reacted with

aluminum chloride the homophenalene 4-methoxy-7-oxo-7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene (XIII) was formed[43]. When the butanoic acid was reacted with stannic chloride in toluene the phenanthrene 6-methoxy-4-oxo-1,2,3,4-tetrahydrophenanthrene was obtained[42]. The conditions of the reaction may also be important. When 1-(7'-methyl-1'-naphthalenyl)propanoic acid was treated with polyphosphoric acid for 45 minutes at 140° the main product was 9-methyl-1-oxo-1-H-phenalene. When the same acid was reacted for only 15 minutes at 110-120° the main product was 2,3-dihydro-9-methyl-1-oxo-1-H-phenalene. The more severe conditions in the former case were shown to have brought about dehydrogenation of the initial dihydrophenalene product[48]. Aluminum chloride will also cause dehydrogenation in 2,3-dihydrophenalenes[43]. Presumably the electron deficient aluminum chloride extracts a hydride from the carbon α to the naphthalene ring. If a 2,3-dihydrophenalene product is desired it is important that these dehydrogenating conditions are avoided as hydrogenation of 2,3-dihydrophenalenes is effected only with extreme difficulty[49].

The nitro-acetoxylation of aromatic compounds

Fischer *et al*[50] have shown that when a series of methyl benzenes is nitrated using mixtures of nitric acid and acetic anhydride the nitro methyl benzene products are

accompanied by significant amounts of acetoxy methyl benzenes. An acetoxy product has been claimed to have been obtained from the nitration of 1-methylnaphthalene[51].

There have been mechanisms suggested for acetoxylation under these nitrating conditions. A kinetic investigation showed that both the nitration and acetoxylation reactions of *o*-xylene were of zeroth order with respect to hydrocarbon[52]. It also showed that the ratio of the rates of nitration and acetoxylation was constant during the reaction, and independent of the rates of the individual (nitration and acetoxylation) reactions. Further, the reaction was accelerated by small quantities of sulphuric or acetic acids, and decelerated by small quantities of lithium nitrate. These results were said to imply that protonated acetyl nitrate was the attacking species, as the constancy of the relative rates of nitration and acetoxylation requres a common acetoxylating and nitrating agent (or a common precursor), and the great acceleration produced by sulphuric acid points to a protonated species. Since nitric acid in an excess of acetic anhydride exists almost entirely as acetyl nitrate, the suggestion that protonated acetyl nitrate is the electrophile seemed reasonable. The following mechanism was suggested, with the protonation of the acetyl nitrate as the rate-determining step accounting for the reaction being

of zeroth order in hydrocarbon:

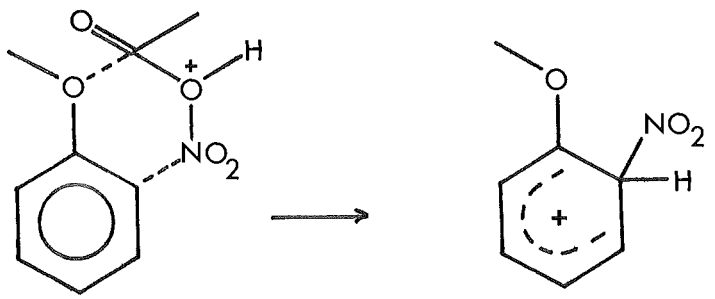
$$HNO_3 + Ac_2O \rightleftharpoons HOAc + AcONO_2$$

$$AcONO_2 + HOAc \rightleftharpoons AcONO_2H^+ + OAc^- \quad \text{(slow)}$$

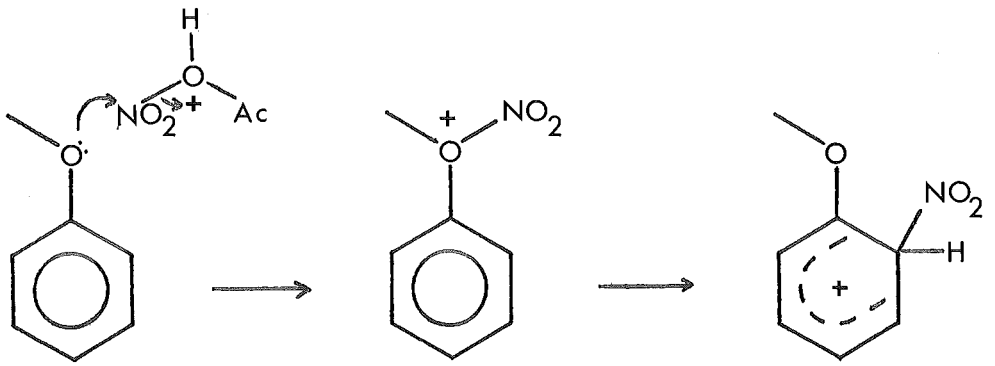
$$AcONO_2H^+ + ArH \longrightarrow ArOAc + ArNO_2$$

Further suggested evidence that protonated acetyl nitrate is the reactive species is the anomalously high *ortho*:*para* ratios obtained in the nitration of some substrates by nitric acid in acetic anhydride. The reactions of anisole, acetanilide, and methylphenethyl ether[53,54], for example, with nitric acid-acetic anhydride give *ortho*:*para* ratios of 1.8-2.5, whereas reactions with mixed acid, or with nitric acid alone give *ortho*:*para* ratios of 0.25-0.7. In contrast, the reactions of other substrates (e.g. toluene or t-butylbenzene) give closely similar *ortho*:*para* ratios with all nitrating systems. It appears that the necessary structural feature for this kind of orientational change, which also occurs on nitration with other acyl nitrates, or with N_2O_5, in organic solvents, is a lone pair of electrons on the substituent near to the ring. It has been proposed that this lone pair provides a site for initial reaction, followed by migration to the nearest

position (the *ortho* position) on the ring. Two mechanisms have been suggested (equations (1)[55] and (2)[54,56])



(1)

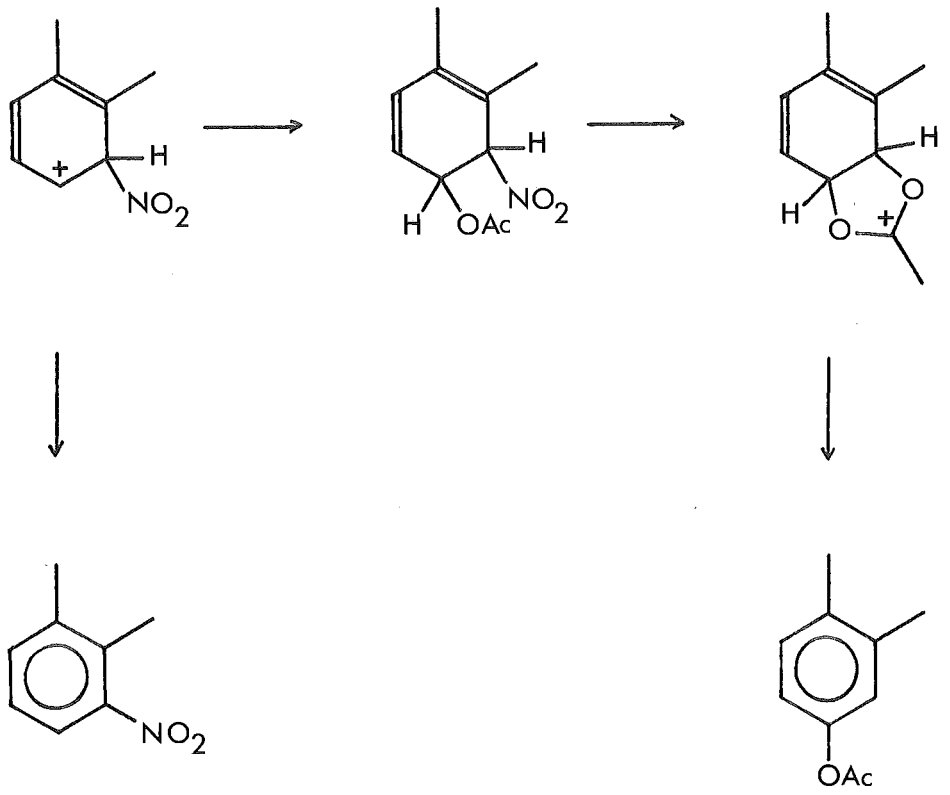


(2)

This mode of specific *ortho* attack must operate in conjunction with normal nitration, which may still involve NO_2^+ attack[57,58].

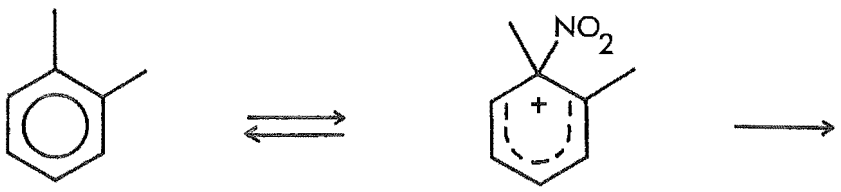
Recently another interpretation of the results of Fischer *et al* was put forward[59]. There is a close similarity between the relative rates and product distributions in

nitration by nitric acid in acetic anhydride, and by nitric acid in other organic solvents like nitromethane and acetic acid. This suggests a common nitrating agent in these systems, and it is evident that this cannot be protonated acetyl nitrate. For this reason, an addition-elimination pathway for acetoxylation, not necessarily involving protonated acetyl nitrate, has been suggested[59a,58].

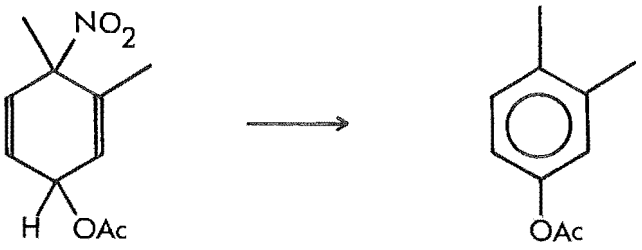


More recently, Blackstock has shown that aromatic acetoxy compounds isolated from the nitration of methyl

benzenes are formed from the decomposition of 1,4 nitro-acetoxy adducts of the benzenes[60]. Using mild reaction conditions and separation techniques he was able to isolate the adducts (e.g. XVII) and then decompose them thermally, or by treatment with acetic acid, to their corresponding aryl acetates (e.g. XVIII). His suggested mechanism is the following:



XVI



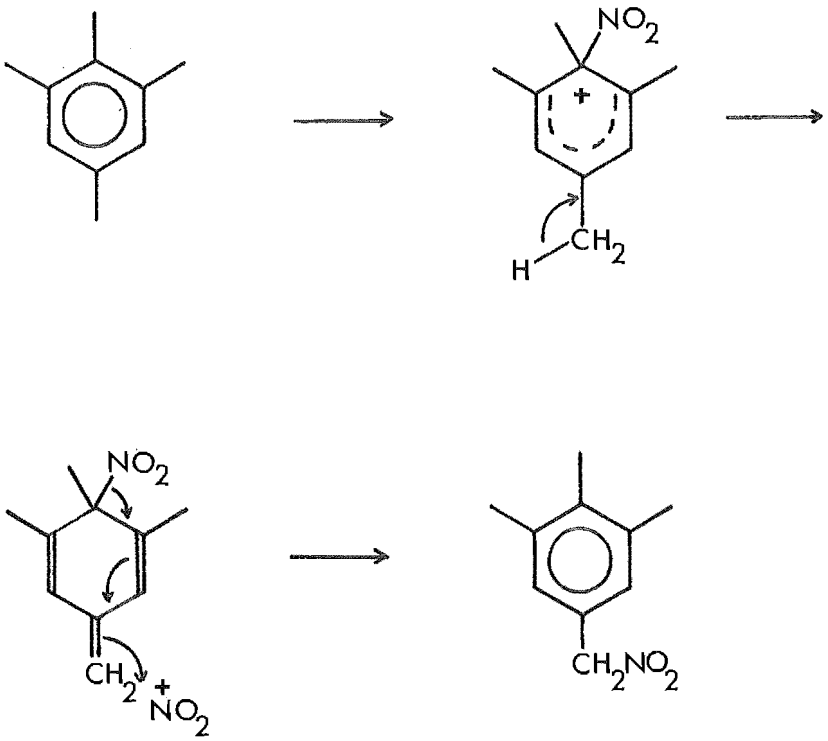
XVII XVIII

The presence of the nitro group attached to a tertiary carbon atom in the cyclohexadiene XVII indicated that the initial reaction was by electrophilic attack on the

aromatic ring. The Wheland intermediate XVI would not be free to rearomatise via the loss of a proton which is the case for unsubstituted positions. Instead it can add an acetoxy group *para* to the nitro group, and form a 1,4 substituted cyclohexadiene (XVII). Both *cis* and *trans* stereoisomers of the cyclohexadienes are formed. This suggests that protonated acetyl nitrate may not be the nitrating species for both *trans* and *cis* isomer formation. If protonated acetyl nitrate were the nitrating species, then it is probable that the acetic acid molecule liberated during the nitration step would not be completely dissociated from the carbonium ion XVI. Instead, it would add at the *para* position to form the diene. Such a mechanism would lead to *cis* diene only, and would hardly account for the claimed predomination of *trans* isomer found in all of the reaction mixtures studied. Blackstock suggests that *cis* addition may proceed via this mechanism while *trans* addition may proceed by another. (This was the conclusion reached by De la Mare *et al* for the formation of dichloro adducts of phenanthrene[59b], and tetrachloro adducts of naphthalene[61].) He claimed to have found evidence for all three of acetyl nitrate, acetic acid, and acetic anhydride to act as the nucleophile at the second step of the addition, although there was difficulty in rigorously ruling out the presence of more than one of these in the reaction mixture

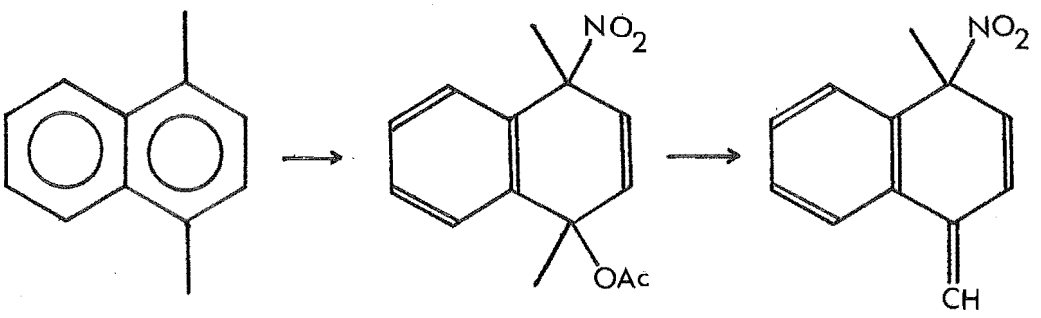
at any one time.

Another reaction which may accompany the nuclear nitration of aromatic compounds is side-chain nitration. Blackstock has noted[58] that the methyl benzenes for which side-chain nitration is observed all have a methyl group *para* to the most activated methyl-substituted ring position, and that the hydrocarbons which do not have this substitution pattern do not afford the products of side-chain nitration. He accounts for this by the mechanism:

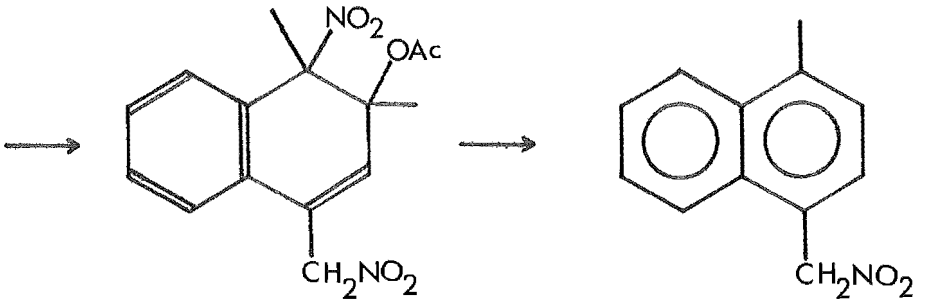


A related mechanism for side-chain nitration in which the Wheland intermediate gives rise to a 1,4 diene

which loses acetic acid to give an *exo*-cyclic methylene group was suggested by Robinson[62] for the formation of 1-methyl-4-nitromethylnaphthalene (XX) from 1,4 dimethyl-naphthalene:



XIX



XX

Fischer and Wilkinson[63] have isolated the diene intermediate XIX by quenching the reaction at low temperatures, and have shown by n.m.r. studies that the diene disappears as the nitromethylnaphthalene XX is formed.

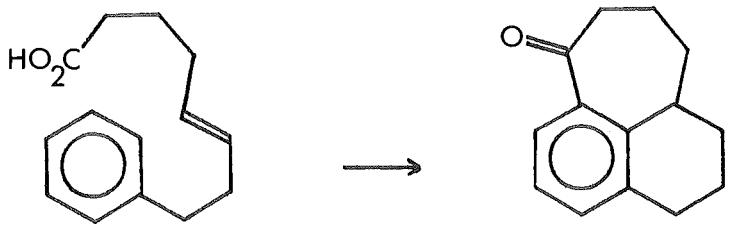
From the more recently suggested mechanisms of

Blackstock it can be seen that the Wheland-type carbonium ion is intermediate in the formation of both aryl acetates and side-chain nitro compounds. It follows, then, that the formation of these compounds should be competitive. This appears to be the case, for some substituted benzenes produce mainly phenylacetates, while others produce phenylnitromethanes. Other than the generalisation that heavily substituted methyl benzenes prefer phenylnitromethane formation, there appears to be no factor which favours this formation over acetate formation[58].

OUTLINE AND DISCUSSION OF SYNTHETIC APPROACHES

The Synthesis of *5,6,7,8-Tetrahydrocyclohepta[de]naphthalene* (**5**)

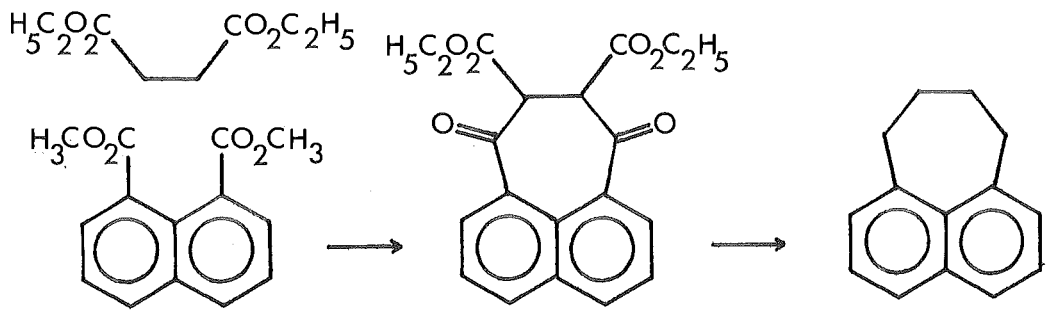
Pleiadane (**5**) was required as the precursor for an attempt to prepare dipleiadane (**17**). There are many possible approaches to its synthesis. The shortest routes involve starting with a substituted naphthalene and constructing the seven-membered ring. Another approach uses benzo cyclic ketones such as α-tetralone (**32**) and benzsuberone (**22**) as precursors for the building of a seven- or six-membered ring as the third ring (see scheme III). Gilmore and Horton[46] synthesised pleiadane from both of these ketones, achieving a yield of 35% from α-tetralone, but only 3.8% from benzsuberone. We did not use the Gilmore and Horton synthesis which started with α-tetralone because this ketone was not available to us at the time. The third approach to pleiadane involves the synthesis of a benzo compound substituted with an aliphatic chain which may be closed at two points in the benzene ring to form two more rings. An example of this type of compound is *trans*-8-phenyloct-5-enoic acid **1**, which may be cyclized to the tricyclic ketone **2** using polyphosphoric acid[64]. The synthesis of **1** is prolonged and of poor overall yield so this route was not attempted.



1 2

Using these three general approaches the following syntheses of pleiadane were investigated.

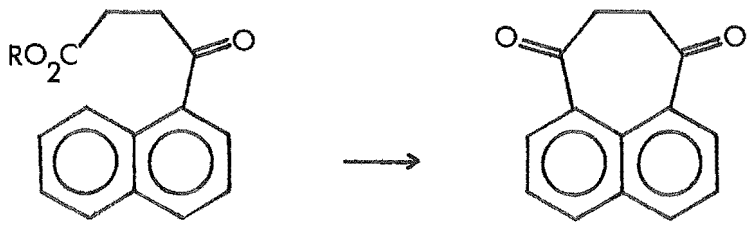
A double Dieckmann condensation of *dimethyl naphthalate* (**3**) with diethyl succinate was attempted. The hoped-for product from this condensation, the diketodiester **4** , was



3 4 5

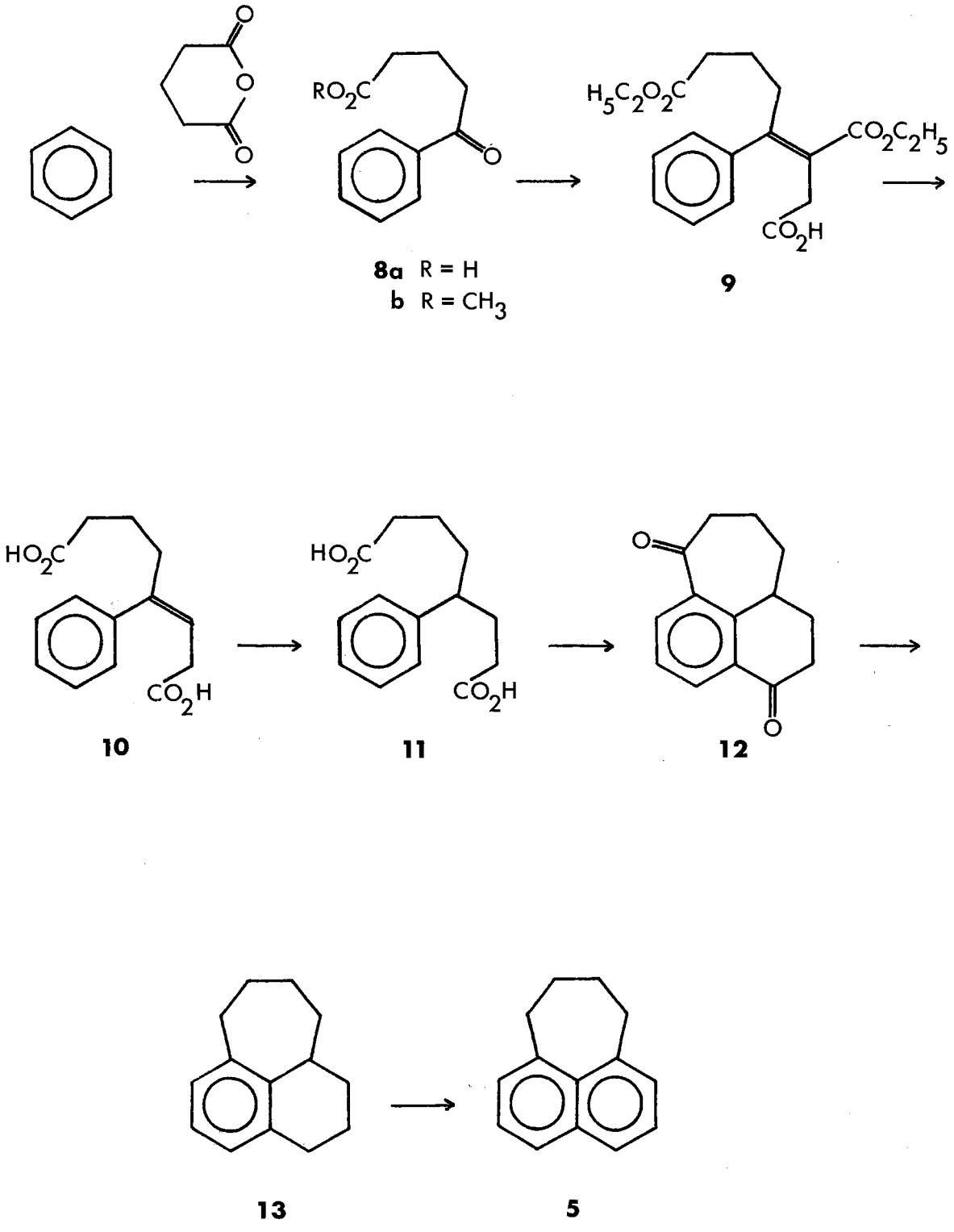
then to be subjected to hydrolysis, decarboxylation, and reduction to form pleiadane (**5**). However, despite Dieckmann's success in cyclizing diethyl succinate and dimethyl glutarate to form a seven-membered ring[65], the condensation would not occur.

The second method attempted also started with a naphthalene derivative and involved the cyclization of *methyl 4-(1'-naphthalenyl)-4-oxobutanoate* (**6b**) to the diketone **7**. The acid 6a was prepared by the Friedel-Crafts condensation of naphthalene and succinic anhydride. When nitrobenzene was used as the solvent a yield of only 28% of the 1'-isomer was achieved, but when 1,2 dichloroethane was used the yield was increased to 70% with very little of the 2'-isomer being produced. This may be explained in terms of the dichloroethane solvating the succinic anhydride-aluminium chloride complex but not the product naphthalenyl butanoate-aluminium chloride complex, and hence the latter does not have the opportunity to rearrange from the kinetically favoured 1'-isomer to the thermodynamically favoured 2'-isomer. Nitrobenzene, however, does solvate the product complex and hence allows isomerisation to take place.



6a R = H
b R = CH_3

7



8a R = H
b R = CH_3

9

10

11

12

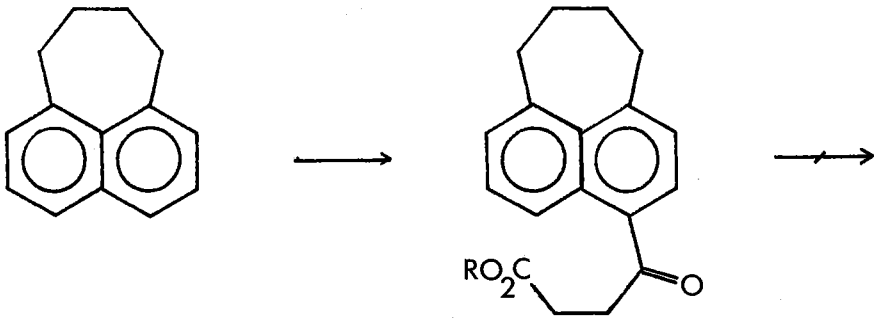
13

5

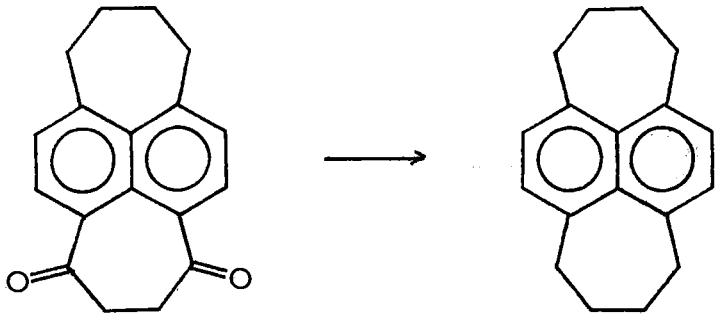
SCHEME I

The ester **6b** was prepared in good yield by esterifying the acid **6a** with methanol-sulphuric acid solution, but it could not be induced to cyclize, even when catalysts as powerful as hot fuming sulphuric acid and sodium chloride-aluminium chloride flux were used.

The third possibility which we explored is outlined in scheme I . This illustrates the third type of approach to pleiadane. Benzene underwent Friedel-Crafts reaction with glutaric anhydride and aluminium chloride to form the keto acid **8a**. This was esterified with methanol-sulphuric acid to the ester **8b** which was then reacted with diethyl succinate under potassium tertiary butoxide catalysis (the Stobbe condensation) to form the diester acid **9** . Refluxing **9** in acetic and hydrochloric acids brought about hydrolysis and decarboxylation to the olefinic diacid **10** . The olefinic diacid **10** was hydrogenated over palladium-on-carbon to the saturated *4-phenyloctanedioic acid* (**11**). This acid was then to be cyclized in one step to the diketone **12** which would then have been reduced by Clemmensen reduction to the hydrocarbon **13** , which in turn would have been aromatised over 30% palladium-on-carbon to form pleiadane (**5**). However, the acid **11** would close only one chain at a time. The failure of both chains to close at the same time necessitated the repetition of the reduction and cyclization steps. The addition of these steps to an already lengthy synthesis



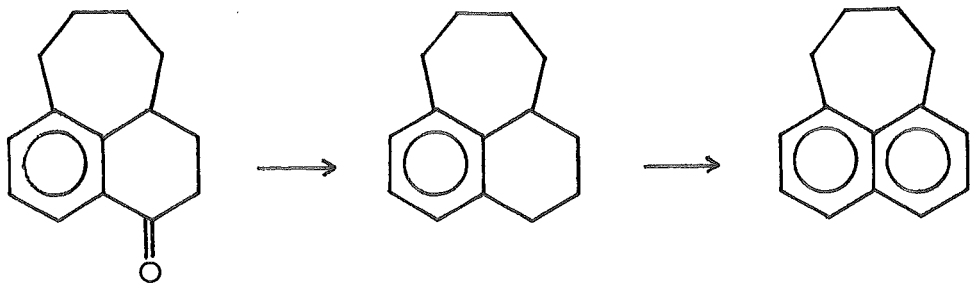
5 **15a** R = H
b R = CH_3



16 **17**

made this route unfavourable, and it was consequently abandoned.

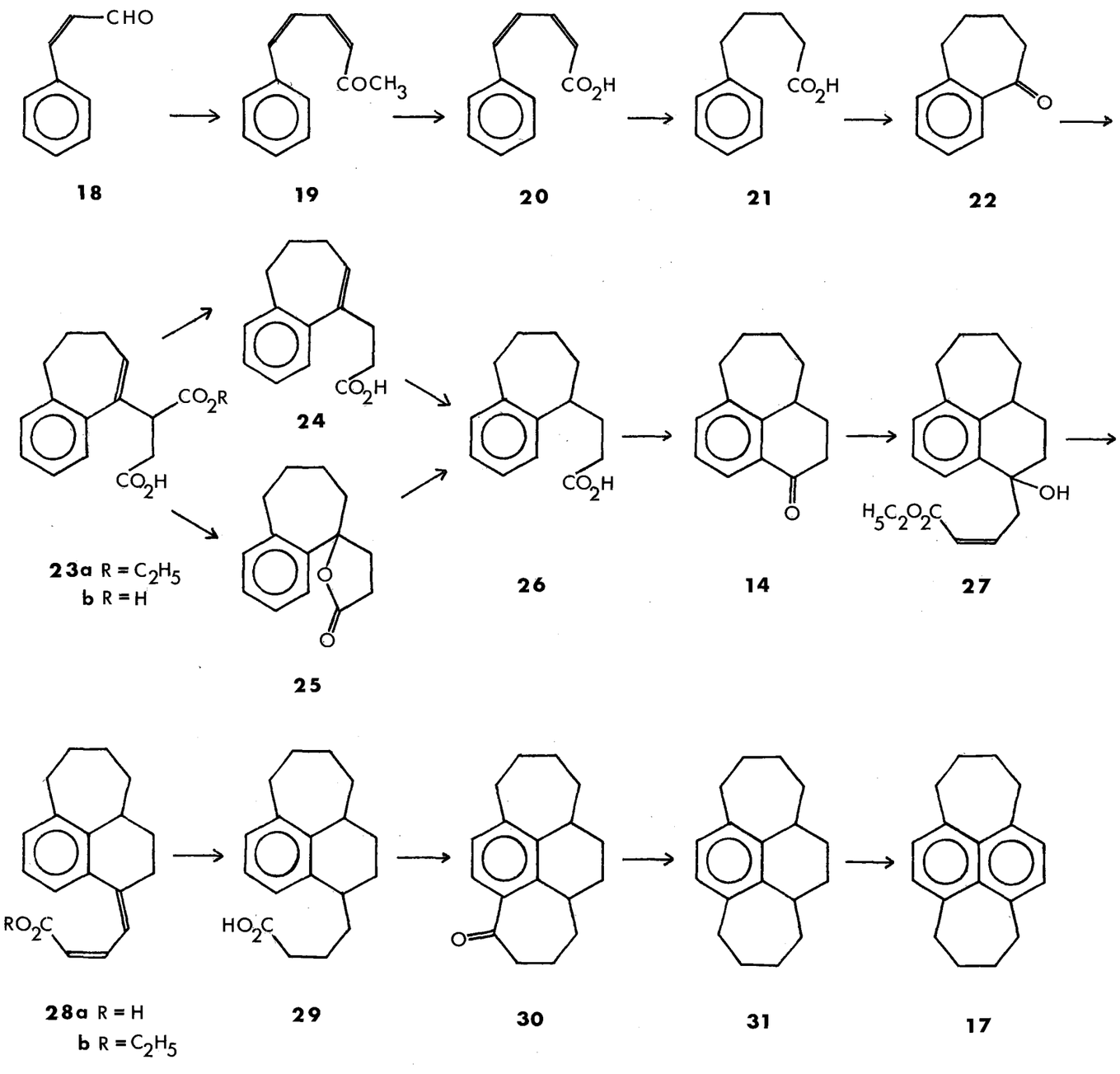
Pleiadane was finally prepared in good yield from benzsuberone via the tricyclic ketone *3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de]naphthalene* (**14**). For the synthesis of **14** from benzsuberone see scheme II and related discussion. When the ketone **14** was subjected to Clemmensen reduction it gave the hydrocarbon **13** which was then aromatised using 30% palladium-on-carbon to pleiadene (**5**).



14 **13** **5**

The Synthesis of *1,2,3,4,7,8,9,10-Octahydrodicyclohepta[de,ij]naphthalene* (**17**)

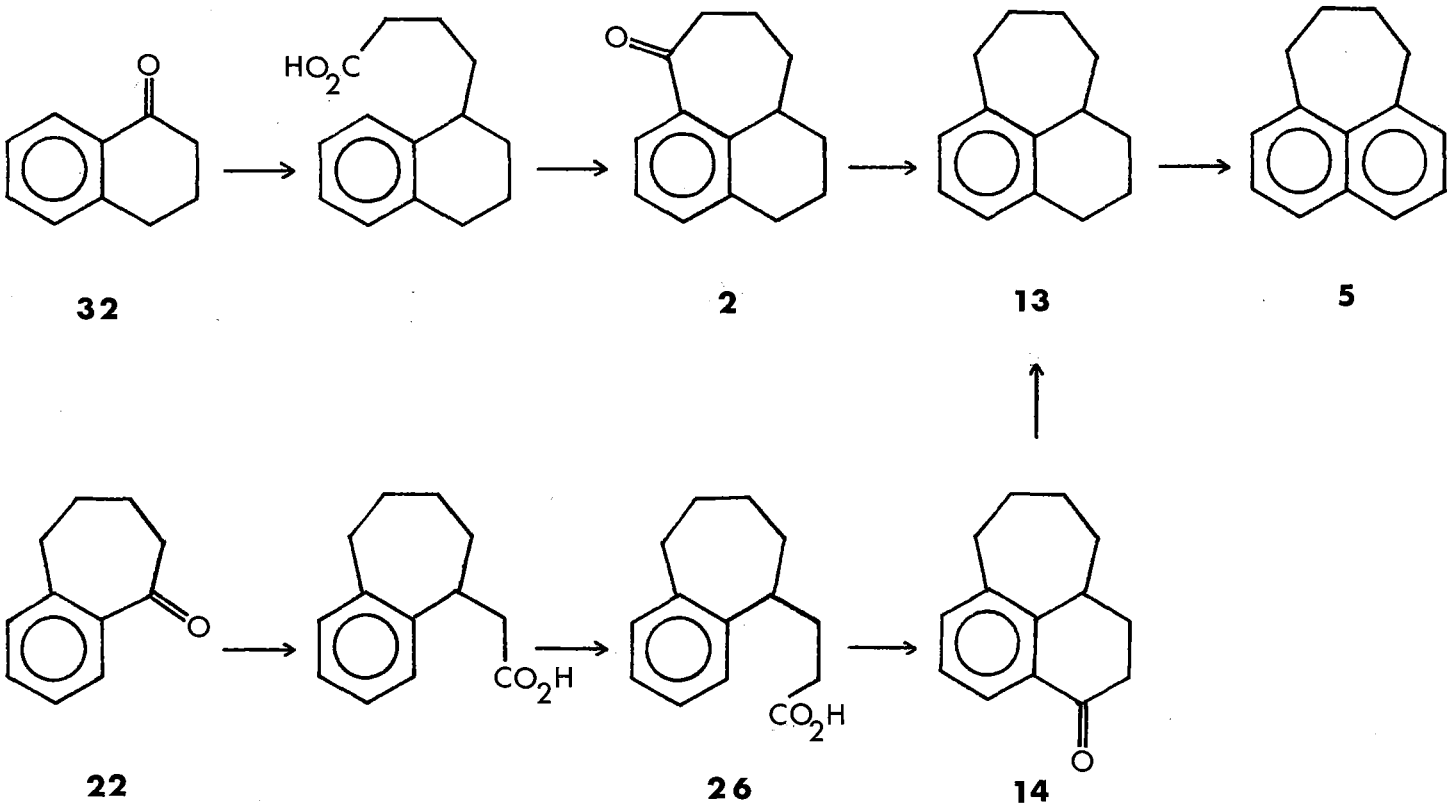
Two approaches to the synthesis of dipleiadane (**17**) appeared to be plausible. The less elaborate scheme started with pleiadane (**5**) and substituted a seven-membered ring at the *peri*-positions. For this route we had as a guide Fieser and Peters' synthesis of 5,6,7,8-tetrahydrocyclohepta[*fg*]acenaphthene[39] (**57**). Pleiadane (**5**)


CHO
COCH3
CO2H
CO2H
O
18
19
20
21
22
CO2R
CO2H
CO2H
24
CO2H
O
OH
H5C2O2C
23a R = C2H5
b R = H
O
O
25
26
14
27
RO2C
HO2C
O
28a R = H
b R = C2H5
29
30
31
17

SCHEME II

was succinoylated using aluminium chloride and succinic anhydride in nitrobenzene to the keto-acid **15a**. Probably a better yield would have resulted if dichloroethane had been used as the solvent, as was later seen for the succinoylation of acenaphthene (**54**). The acid was esterified to its methyl ester **15b** which was then subjected to the action of molten aluminium and sodium chlorides in the hope of bringing about an intramolecular Friedel-Crafts reaction to form the diketone **16**, which was then to be reduced to dipleiadane **17**. Unfortunately the ring closure did not take place, and as pleiadane was in short supply this synthesis was not pursued further.

Our second and successful route to dipleiadane finally took the form of that shown in scheme II. Crotonaldehyde (**18**) was condensed with acetone in the presence of sodium hydroxide (an aldol condensation) to form cinnamylidene acetone (**19**). This was oxidized with hypochlorite solution to produce cinnamylidene acetic acid (**20**). Catalytic hydrogenation of **20** gave 5-phenylpentanoic acid (**21**) which was cyclized using polyphosphoric acid for benzsuberone (**22**). Benzsuberone was condensed with diethyl succinate under the influence of potassium tertiary butoxide (a Stobbe condensation) to form the half-ester **23a**. When the half ester was refluxed with hydrochloric and acetic acids it underwent simultaneously hydrolysis



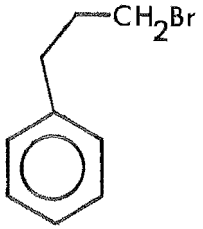
SCHEME III

and decarboxylation to form a mixture of the olefinic acid **24** and its isomeric lactone **25**. These were reduced with hydrogen over palladium-on-carbon and phosphorus and iodine, respectively, to the saturated acid **26**. Treatment of **26** with polyphosphoric acid gave the tricyclic ketone **14**. The ketone was reacted with methyl γ-bromocrotonate in the presence of zinc powder (a Reformatsky reaction) to form the hydroxy olefin ester **27**. When **27** was hydrolysed with base it also underwent dehydration to give the diene acid **28a**. Hydrogenation of **28a** over palladium-on-carbon gave the acid **29** which was cyclized with polyphosphoric acid to the tetracyclic ketone **30**. **30** was reduced by the Clemmensen method to the hydrocarbon **31** which was aromatised over 30% palladium-on-carbon to dipleiadane (**17**). All these steps with the exception of the Reformatsky reaction had optimum yields in the vicinity of 90%.

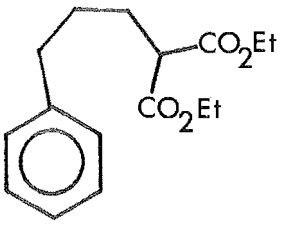
The work of Gilmore and Horton[46] who synthesized pleiadane in two ways (scheme III) was an aid in this synthesis of dipleiadane. In the preferred method the seven-membered ring was built up by adding a four carbon side chain to α-tetralone **32** via a Reformatsky reaction with methyl γ-bromocrotonate; subsequent dehydration, hydrogenation, ester hydrolysis, and ring closure of the acid gave the tricyclic seven-membered ring ketone **2**.

Reduction of the ketone to the octahydrocycloheptanaphthalene **13**, followed by dehydrogenation gave the tetrahydrocycloheptanaphthalene **5** in 35% overall yield. The alternative synthesis started with benzosuberone **22** as the functional bicyclic compound and the required six-membered ring was built up via a Reformatsky reaction using ethyl bromoacetate; subsequent dehydration, reduction, conversion to halide, extension of the chain via Grignard formation and carbonation, and ring closure, gave the tricyclic six-membered ring ketone **14**. Reduction of this ketone gave the same octahydrocycloheptanaphthalene as obtained above and dehydrogenation of this gave the tetrahydronaphthalene in 3.8% overall yield. In our synthesis of dipleiadane we were required to build both six- and seven-numbered rings. Gilmore and Horton's method of building a seven-membered ring is of reasonable yield, but their method of adding a three carbon chain to benzsuberone was of no practical use to us. To overcome this problem we tried to add a three-carbon chain in one step by using a Wittig reaction, but the ketone was reluctant to react. However, when benzsuberone was reacted with diethyl succinate in the presence of potassium tertiary butoxide, 90% of the ketone was converted to the desired product, thus adding in one step a three-carbon chain incorporating a terminal carboxylic acid function which was suitable for closing

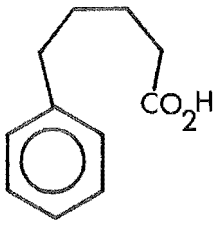
into the benzene ring. Our second problem was that our synthesis started with benzsuberone rather than tetralone, and as this is very expensive and a large quantity would be required for such a lengthy exploratory synthesis, a reasonable method for its preparation was required. The precursor to benzsuberone is 5-phenylpentanoic acid (**21**). This acid may be prepared by the reduction of cinnamylidene acetic acid (**20**), or from the diethyl malonate condensation of 3-phenyl propyl bromide (**33**) followed by hydrolysis and decarboxylation. The latter preparation was found to require more work for a lower yield.



33



34



21

Cinnamylidene acetic acid (**20**) was prepared from cinnamaldehyde (**18**) by three methods. The first employed a Knovenagel condensation with malonic acid using piperidine as the base. The intermediate cinnamylidene malonic acid undergoes spontaneous decarboxylation to give the desired product. The second preparation was via the aldol condensation of cinnamaldehyde and pyruvic acid in the presence

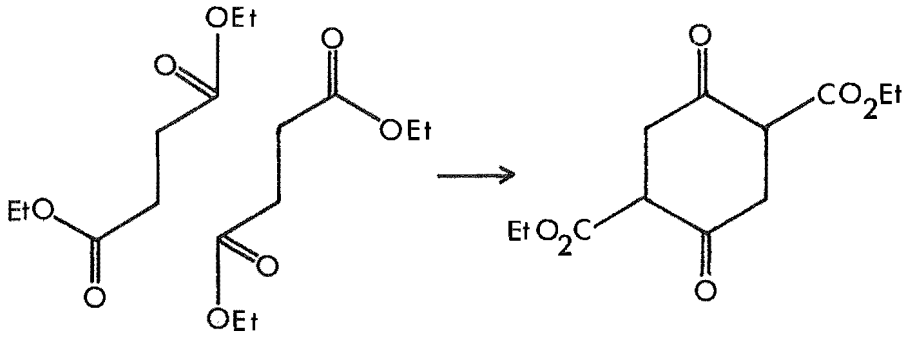
of sodium hydroxide. The resulting cinnamylidene pyruvic acid was oxidised using hydrogen peroxide. The third method used another aldol condensation, that with acetone. The product cinnamylidene acetone was oxidised using hypochlorite solution. The Knoevenagel condensation, after *in situ* reduction, gave only an 11% yield of 5-phenylpentanoic acid. The poor yield was probably due to the Raney nickel reduction step rather than the initial condensation. The aldol condensations gave yields of 39 and 80% respectively, and hence the cinnamaldehyde-acetone condensation was the one used for the large-scale preparation.

5-Phenylpentanoic acid (**21**) was prepared from cinnamylidene acetic acid using both high and low pressure hydrogenation over palladium-on-carbon. Raney nickel is reported to catalyse this reduction in good yield[66], but our attempts using it after activation both *in* and *ex situ* gave poor yields.

Benzsuberone (**22**) was prepared from 5-phenylpentanoic acid using polyphosphoric acid in 50-90% yields. The purity of the pentanoic acid was found to be the critical factor. Polyphosphoric acid has also been used to cyclize esters[67]. Hence we used polyphosphoric acid to cyclize the diester **34** in the hope of short-cutting the synthesis of benzsuberone from 3-phenyl propyl bromide (**33**). However, after hydrolysis-decarboxylation of the cyclization

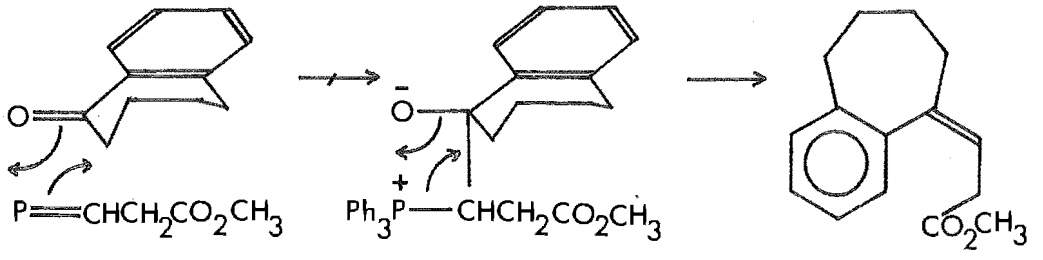
product, the yield of benzsuberone was poor. In view of Cope's success in using aluminium chloride to cyclize the acid chloride of 3-phenylpropanoic acid to 1-indanone[68], this method was attempted, but most of the reactant was recovered as the acid.

3-Carbethoxy-3-(1',2'-benzocyclohepta-1',3'-dien-3'-yl)propanoic acid (**23a**) was first prepared by Cook, Philip, and Somerville[69] in a 58% yield from the Stobbe condensation of benzsuberone with diethyl succinate using potassium tertiary butoxide as the base. Using the same reagents we achieved a yield of 90% with an 8% recovery of benzsuberone. Johnson's conclusions from his work with α-tetralone[70] were confirmed in that the Stobbe condensation between benzsuberone and diethylsuccinate gave better yields with a potassium-tertiary butoxide system than a sodium hydride-ethanol-benzene system. This is probably because the bulky tertiary butoxide ion has less tendency to reduce the highly enolisable and hindered carbonyl group of benzsuberone (or tetralone) than the ethoxide ion, which is the active agent when the sodium hydride system is used. A 1.5 molar excess of diethyl succinate was used to off-set the major side-reaction which is a Dieckmann self-condensation of the succinate:



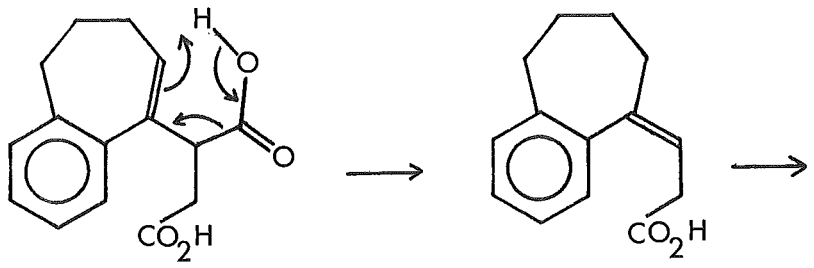
In an attempt to reduce the extent of this side-reaction a reaction was run in which the succinate was added dropwise over an hour, with refluxing, rather than adding it all at once. However, like another run in which the reaction mixture was stood at room temperature for 100 hours, the yield was not improved.

Originally we had intended to use the elegant Wittig reaction to add a three-carbon chain to benzsuberone. Benzsuberone was reacted with the phosphorane liberated from 2-methoxycarbonylethyltriphenylphosphonium iodide:

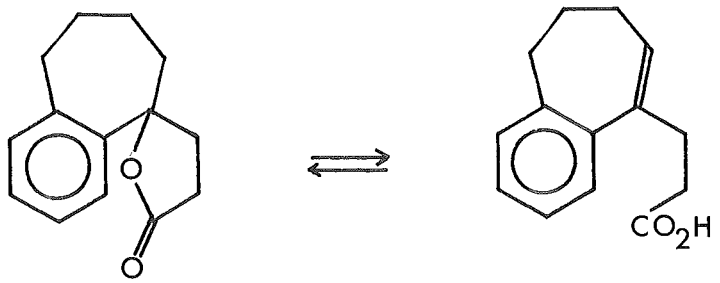


However, despite trying a wide range of reaction conditions with temperatures varying from 0 to 180° and the use of a variety of phosphorane-liberating bases, no product of ketone-ylide reaction was isolated. This was probably due to the hindered stereochemistry of the benzsuberone carbonyl group and to the acidity of its α-protons. Wittig reactions on compounds of similar stereochemistry to benzsuberone have been reported to give reasonable yields[71], but the substrates lacked α-protons, or involved structures which do not give rise to conjugatively stabilised enols.

3-(1',2'-Benzocyclohepta-1',3'-dien-3'-yl)propionic acid (**24**) and the *lactone* of *3-(1',2'-benzo-3'-hydroxy-cyclohepta-1'-en-3'-yl)propionic acid* (**25**) were the major products when the half-ester **23a** underwent hydrolysis and simultaneous decarboxylation. After hydrolysis of the ester function decarboxylation is thought to follow that path **23b → 35 → 25** . The olefinic acid **35** is not isolated owing to its rapid isomerisation to the lactone **25** which then favours isomerisation to the *endo* olefinic acid **24** [72]:



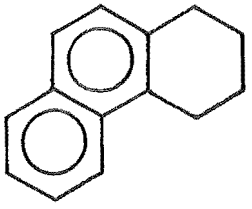
23 **35**



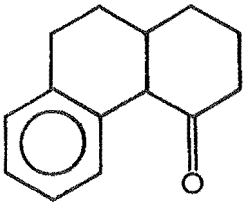
25 **24**

3-(1',2'-Benzocyclohept-1'-en-3'-yl)propionic acid (**26**) has been previously prepared in small quantities by Gilmore and Horton[46], but they were unable to characterise it other than by the m.p. of its amide. We prepared the acid in good yield from the reduction of both the olefinic acid using palladium-on-carbon as catalyst and the lactone using phosphorus and iodine. When crude samples of lactone were reduced considerable amounts of neutral compounds were recovered. When the product of a Stobbe condensation of

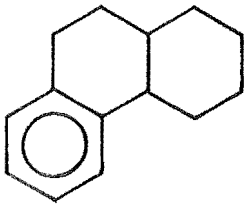
molar proportions was refluxed in acid solution for an unusually prolonged period the neutral compounds which were isolated amounted to 12% of the total product. V.p.c. analysis of the neutral fraction indicated that it comprised five compounds. The two major components were isolated and characterised as *1,2,3,4-tetrahydrophenanthrene* (**36**) and *1,2,3,4,4a,9,10,10a-octahydro-4-oxophenanthrene* (**37**). Spectral data suggested that two of the minor components were *1,2,3,4,4a,5,6,10a-octahydrophenanthrene* (**38**) and unreacted benzsuberone.



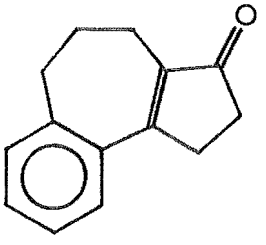
36



37



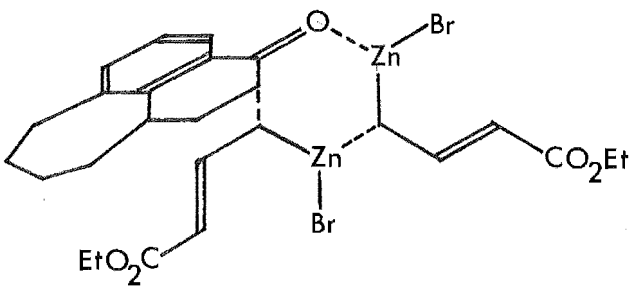
38



39

The tricyclic ketone *3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de]naphthalene* (**14**) was prepared in 90-93% yields when the distilled propionic acid **26** was treated with polyphosphoric acid. Of the other cyclization agents used only hydrogen fluoride was successful. It gave poorer yields than polyphosphoric acid, but this may have been due to the doubtful purity of the propionic acid that was used. Attempts to cyclize the acid via its acid chloride under the catalysis of stannic or aluminium chloride were fruitless. When the propionic acid **26** was contaminated with unreduced olefinic acid **24** the ketone *4,5-benzo-1,2,3,6,7,8-hexahydro-1-oxoazulene* (**39**) was formed as a minor product. This ketone was easily separated from the desired ketone by recrystallizing the cyclization product from methanol, and it was isolated by subjecting the mother liquors to column chromatography. It was found to have spectral characteristics identical to those of the sole product from the reaction of the olefinic acid **24** with polyphosphoric acid. It also had a melting point comparable to the product obtained by Cook *et al* when they subjected the half-ester **23a** to treatment with a mixture of acetic anhydride, acetic acid, and zinc chloride[69]. Obviously the propionyl chain prefers to form a five-membered ring on a double bond rather than a six-membered ring on an aromatic nucleus.

Ethyl 4-(3'-hydroxy-1',2',3,7',8',9',10',10a'-octahydrocyclohepta[de]naphthalene-3'-yl)but-2-enoate (**27**) was prepared from the Reformatsky reaction of the tricyclic ketone **14** with ethyl γ-bromocrotonate in the presence of zinc. The yield was relatively low, but this is characteristic of Reformatsky reactions of this type. The reaction has the advantage of adding a four-carbon chain in one step. Also, the conditions of the reaction are mild enough for the ketone not to be reduced and unreacted ketone may be recovered. Although the reactivity of the Reformatsky reagent is low compared with a Grignard reagent it will react with ketones of low reactivity. This is thought to be due to a six-centred transition state (**40**) which allows for a "push-pull" effect of the potential carbanion and the oxygen-metal complex formation.



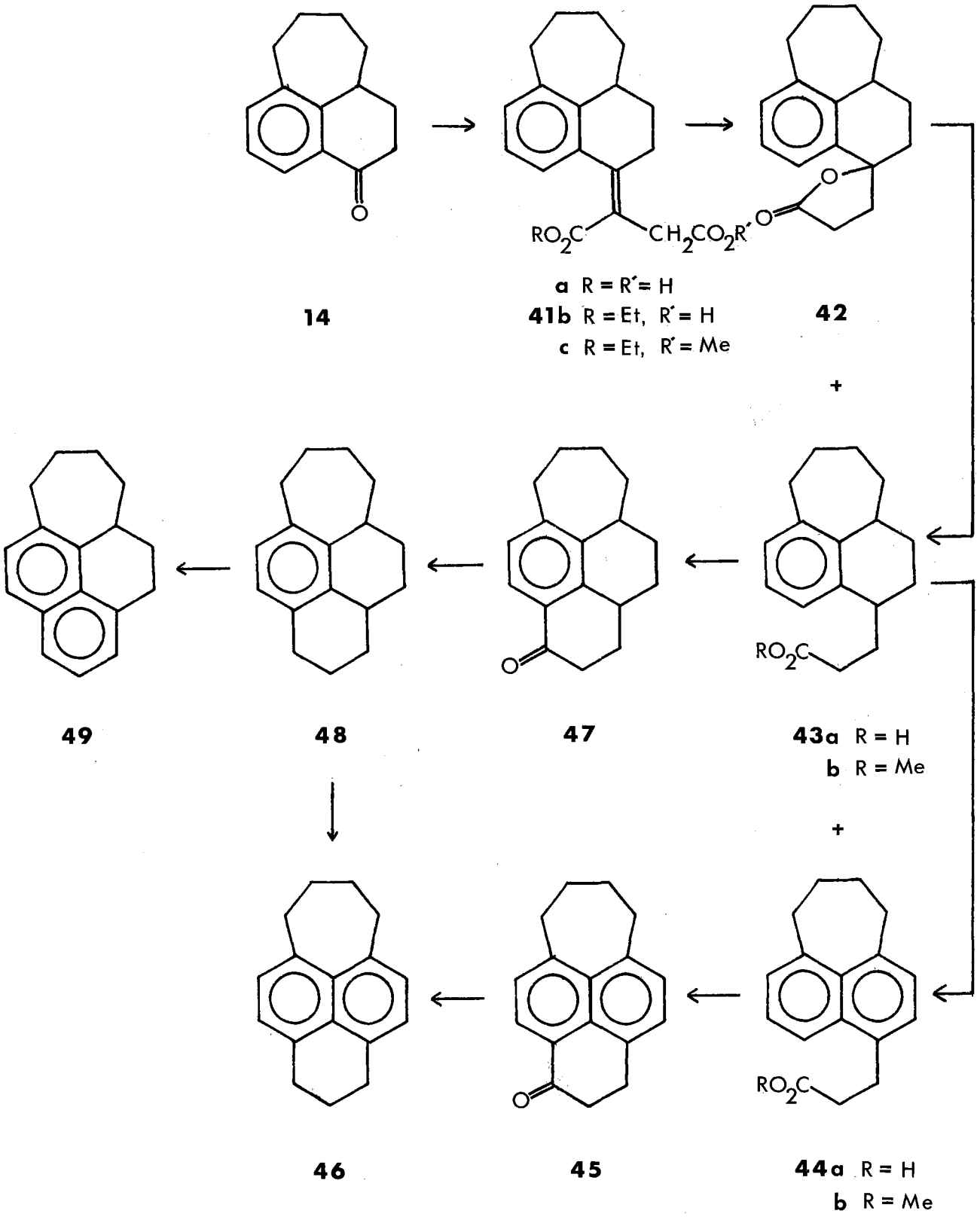
40

The carbonyl function of the tricyclic ketone **14** is of low reactivity because it is conjugated with the aromatic nucleus and it is also sterically hindered. As the reactivity of the carbonyl function of the ketone decreases it approaches the reactivity of the carbonyl function of the ester group of the Reformatsky reagent. This causes the self-condensation of the Reformatsky reagent to compete with the desired reaction. This and other side reactions of the reagent may be overcome by periodic additions of zinc and crotonate over a lengthy reaction period. In this manner the method of Gilmore and Horton[46] was followed. More recently Vaughan *et al* were able to prepare the organo-zinc Reformatsky reagent and then titrate it against fluorenone. This method of prior formation of the Reformatsky reagent before addition of the ketone substrate was attempted, but only a small yield of the desired product was obtained. An attempt to ascertain the amount of active reagent present by titrating the bromozinc crotonate against fluorenone also failed because the highly-coloured complex masked the disappearance of the fluorenone coloration.

4-(1',2',3',7',8',9',10',10a'-Octahydrocyclohepta[de]naphthalen-3'-ylidene)but-2-enoic acid (**28a**) was prepared from the hydroxy ester **27** in two ways. The first followed the route of Gilmore and Horton[46] who reacted

α-tetralone with methyl γ-bromocrotonate and separated unreacted starting material from the product by distillation, effecting simultaneous dehydration of the hydroxy butenoate (a compound similar to **27**). We found that the tricyclic ketone would not separate cleanly from the product and the high temperatures required for the distillation produced charring. Despite these high temperatures not all the hydroxy ester was dehydrated, although dehydration might have been achieved if a crystal of iodine had been placed in the still pot[75]. Dehydration was completed using phosphorus oxychloride in pyridine. The diene ester **28b** was then hydrolysed to its acid using concentrated alkali solution. The second route followed was that of hydrolysing the crude Reformatsky product with cold concentrated hydroxide-ethanol mixtures and collecting the base-soluble product. It was found that dehydration occurred during the hydrolysis step, so that the desired dienic acid was obtained from the crude Reformatsky product in one step.

4-(1',2',3',7',8',9',10',10a'-Octahydrocyclohepta[de]naphthalen-3'yl)butanoic acid (**29**) was produced in good yield from the catalytic hydrogenation of the dienic acid **28a** , and after recrystallisation it was cyclized to the tetracyclic ketone *1-oxo-1,2,3,4,4a,5,6,6a,7,8,9,10-dodecahydrodicyclohepta[de,ij]naphthalene* (**30**) using


RO2C
CH2CO2R'
O
a R = R' = H
41b R = Et, R' = H
c R = Et, R' = Me
14
42
+
43a R = H
b R = Me
47
48
49
+
44a R = H
b R = Me
45
46

SCHEME IV

polyphosphoric acid.

1,2,3,4,4a,5,6,6a,7,8,9,10-Dodecahydrodicyclohepta[de,ij]naphthalene (**31**) was formed when the tetracyclic ketone **30** underwent Clemmensen reduction. When **31** was aromatised over 30% palladium-on-carbon the final product *1,2,3,4,7,8,9,10-octahydrodicyclohepta[de,ij]naphthalene* (**17**) was obtained. The optimum overall yield of from cinnamaldehyde was 6%.

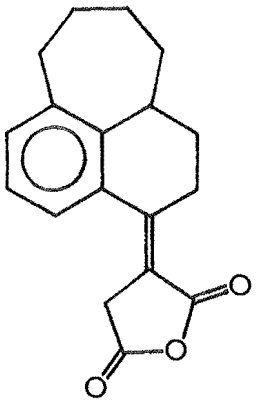
The Synthesis of *2,3,6,7,8,9-Hexahydro-1H-cyclohepta[gh]phenalene* (**46**)

Peripleiadane (**46**), homologous to dipleiadane (**17**), was synthesised by the route shown in scheme IV. For the preparation of the tricyclic ketone **14** see scheme II.

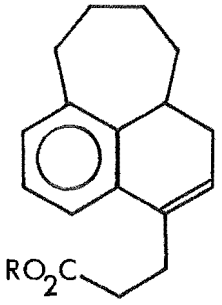
The Stobbe condensation of 3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**) with diethyl succinate gave the *exo* olefinic half-ester 3-carbethoxy-3-(1',2',3',7',8',9',10',10a'-octahydrocyclohepta[*de*]napthalen-3'-ylidene)propionic acid (**41b**). Acid catalysed hydrolysis and concurrent decarboxylation of the half-ester **41b** produced the lactone of 3-(3'-hydroxy-1',2',3',7',8',9',10',10a'-octahydrocyclohepta[*de*]naphthalen-3'-yl)propionic acid (**42**) together with 3-(1',2',3',7',8',9',10',10a'-octahydrocyclohepta[*de*]naphthalen-3'-yl)propionic acid (**43a**) and 3-(7',8',9',10'-tetrahydrocyclohepta[*de*]naphthalen-3'-yl) propionic acid (**44a**). On refluxing in acetic acid with

red phosphorous and iodine, the lactone **42** was converted into a mixture of the octahydro acid **43a** and tetrahydro acid **44a** . The mixture of acids **43a** and **44a** was converted into a mixture of the methyl esters **43b** and **44b** by treatment with diazomethane. The octahydro ester **43b** component of the mixture was dehydrogenated and essentially pure tetrahydro ester **44b** was obtained by heating the mixture with palladium-on-charcoal. Treatment of the ester **44b** with anhydrous hydrogen fluoride brought about ring closure and gave an excellent yield of 1-oxo-2,3,6,7,8,9-hexahydro-1H-cyclohepta[*gh*]phenalene (**45**). Clemmensen reduction of the ketone **45** gave the desired hexahydrocyclohepta[*gh*]phenalene **46** , obtained in 49% overall yield from the ketone **14** .

The Stobbe condensation of the ketone **14** was catalysed by potassium tertiary butoxide and was similar to the Stobbe condensation of benzsuberone (**22**) and α-tetralone, in which yields of 90% and 94%[70] were attained. However, despite the similarity in structure of the tricyclic ketone **14** to these two ketones, an optimum yield of only 82% was achieved. The half-ester **41b** could not be crystallized so it was esterified using diazomethane to the diester **41c** and hydrolysed to the diacid **41a** in order that it could be characterised. When the diacid **41a** was sublimed the anhydride **50** was formed.



50



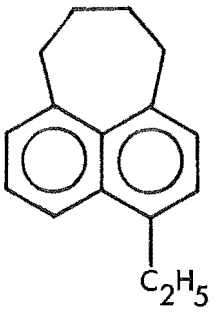
a R = H

51b R = CH_3

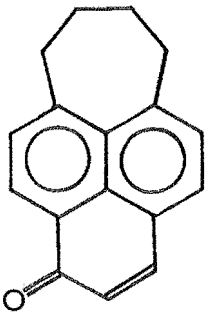
Hydrolysis-decarboxylation of the half-ester was expected to lead to a mixture of the lactone **42** and its isomeric olefinic acid **51a** . The olefinic acid **51b** could be detected as its methyl ester **51b** , after methylation with diazomethane of a sample of the reaction mixture isolated after a reaction of short duration. However, only the lactone **42** and the disproportionation products, **43a** and **44a** , of the olefinic acid were obtained from the reactions of extended period. The tetrahydro acid **44a** was much less soluble than the octahydro acid **43a** and almost pure acid **44a** crystallized out from the hydrolysis mixture, as was shown by methylation with diazomethane and vapour phase chromatography (v.p.c.) of the ester mixture.

When the lactone **42** was reduced with red phosphorus and iodine, besides the expected acid **43a** , the fully aromatized

acid **44a** was also obtained. When the acidic products had been extracted from the lactone reduction a minor neutral fraction remained. Other than a small amount of unreduced lactone three compounds were detected: the ketone **47** , the hydrocarbon **52** , and the anhydride **50** . These compounds are likely to have been formed by the acid-catalysed ring closure of the acid **43a** , the decarboxylation of the acid **44a** , and the dehydration of the diacid **41a** respectively. **43a** and **44a** are products of the hydrolysis-decarboxylation of the half-ester **41b** , and **41a** is an intermediate compound, so it is likely that the compounds **47** , **52** , and **50** were formed under the strongly acidic conditions of this reaction but because of their neutral character were not isolated until after the lactone reduction step.



52

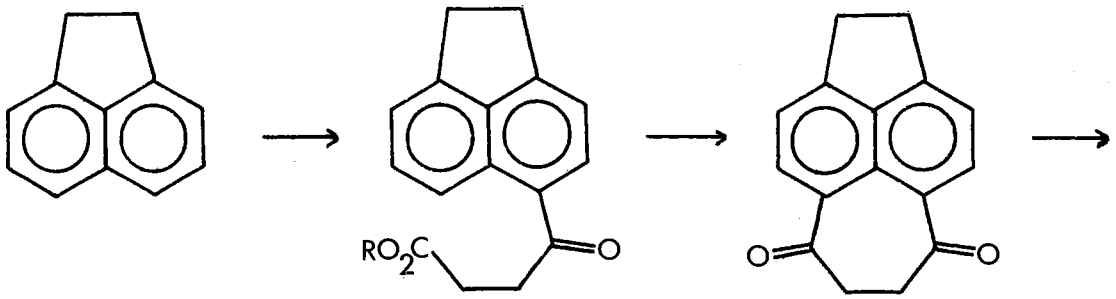


53

In an attempt for form the acid **44a** by the aromatisation of **43a** considerable decarboxylation took place

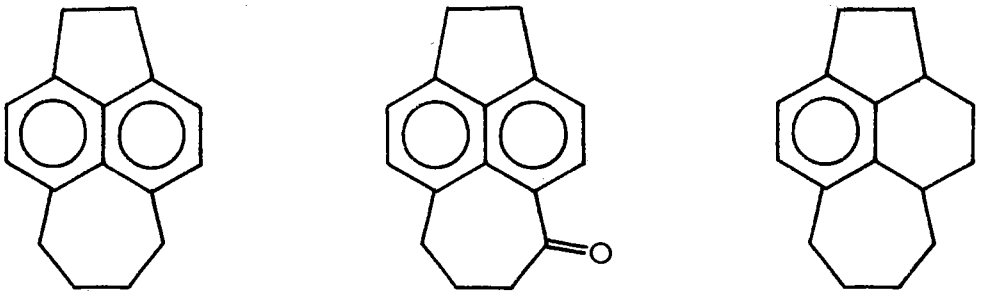
leading to the formation of the hydrocarbon **52** . The methyl ester **43b** was less prone to undergo decarbomethoxylation and in a reaction which gave an otherwise quantitative yield of the fully aromatic ester **44b** only 5% of 3-ethyl pleiadane (**52**) was obtained. Similar observations were made by Newman and O'Leary for the aromatisation of 5,6,7,8-tetrahydro-2-naphthylacetic acid and its methyl ester[76]. The ester **44b** was much more soluble in hydrogen fluoride than the acid **44a** and was therefore much more suitable as a substrate for the ring closure reaction to give the ketone **45** . When the condensation of the ester **44b** with hydrogen fluoride was carried out for reaction times longer than 3 hours, or when polyphosphoric acid was used as the condensing agent the ketone **45** was contaminated with the enone **53** . With polyphosphoric acid the enone **53** was the major product and a considerable amount of tar was also formed. The ketone **45** was also readily dehydrogenated to enone **53** with dichlorodicyanoquinone, and the reverse reaction was achieved quantitatively by low pressure hydrogenation over platinum.

The Clemmensen reduction of the ketone **45** to give the desired hydrocarbon **46** was conducted for a much shorter time than is traditionally used for this reaction because the reduction was rapid and it was found that prolonged treatment of either **45** or **46** with acid led to the formation of the enone **53** and its subsequent dimerisation.



54 **55a** R = H **56**

b R = CH_3



57 **58** **59**

SCHEME V

Catalytic reduction of the ketone was attempted but it gave poor yields of **46**.

In the preparation of 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*]naphthalene the fourth (seven-membered) ring was constructed before the second six-membered ring was aromatised. This was necessary since ring closure would have otherwise preferentially occurred in this second aromatic ring and a cycloheptaphenanthrene system formed[72]. Initially, we attempted to follow the same sequence for the preparation of the cycloheptaphenalene **46**. Ring closure of the ester **43a** with polyphosphoric acid gave the ketone **47** in excellent yield. Clemmensen reduction of the ketone **47** gave the hydrocarbon **48**. Dehydrogenation of hydrocarbon **48**, by heating with palladium-on-carbon gave as major product (73%) the hydrocarbon **49** together with a lesser amount (23%) of the desired hydrocarbon **46**. The ketone **47** was dehydrated and dehydrogenated, by heating palladium-on-carbon, to the same mixtures of hydrocarbons.

The Synthesis of *5,6,7,8-Tetrahydrocyclohepta[fg]acenaphthene* (**57**)

L. F. and M. A. Fieser[39] first synthesised this compound forty years ago by the route shown in scheme V. The keto acid **55a** was formed by the Friedel-Crafts reaction of the acenaphthene (**54**) with succinic anhydride. Its

ester **55b** in the presence of molten aluminium and sodium chlorides underwent an intramolecular Friedel-Crafts reaction to form the diketone **56** , which was then reduced to the desired hydrocarbon **57** by the method of Wolff-Kishner. Duplicating Fieser's conditions, the final product was obtained in an overall yield of only 13%. The synthesis has the virtue of containing only four steps, and minor changes in the reaction conditions and isolation procedures increased the overall yield to 35%.

In the Friedel-Crafts reaction of the first step the yield was increased slightly and the reaction made considerably less arduous when the solvent nitrobenzene was replaced by 1,2-dichloroethane. The advantage of dichloroethane over nitrobenzene in this type of reaction is that nitrobenzene dissolves not only the aluminium chloride-acylating agent complex but also the product ketone-aluminium chloride complex, and hence allows for reaction reversibility and a build-up of the more thermodynamically stable 3-isomer, while dichloroethane on the other hand dissolves the product complex only sparingly[77]. However, the main advantage of using dichloroethane is that it is quickly and cleanly evaporated at the end of the reaction, as opposed to a prolonged steam distillation required to rid the reaction mixture of nitrobenzene.

The intramolecular Friedel-Crafts reaction with

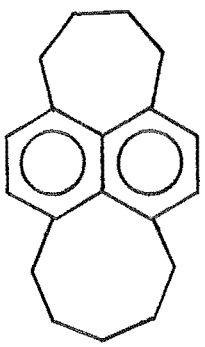
molten aluminium and sodium chlorides produces much tar and has a rather poor (43%) yield of the diketone **56** . Other cyclization agents such as anhydrous hydrogen fluoride and aluminium chloride in refluxing dichloroethane were tried, but these were unsuccessful. The only innovation which improved Fieser's method was that of purifying the crude product by chromatography rather than by distillation, the latter requiring high temperatures. The column eluants were quite pure, and were purified further by sublimation.

The hydrocarbon **57** was prepared from the diketone **56** by three methods. Fieser's observations that the Clemmensen reduction of the diketone is unsuccessful, but that it may be reduced by the Wolff-Kishner method, were confirmed, although using the latter a yield of only 50% could be achieved. This yield was improved to 74% when a lower temperature, modified Wolff-Kishner reduction was used in which the dihydrazene was prepared and isolated before being subjected to treatment with tertiary butoxide in refluxing toluene. A room temperature dimethyl-sulphoxide reduction in the manner of D. J. Cram *et al* was also attempted but this was unsuccessful. The cleanest and highest yielding (95%) conversion of diketone to hydrocarbon was achieved catalytically using palladium-on-carbon. This reduction proceeds smoothly so long as the uptake of hydrogen is measured accurately. A deficiency of hydrogen

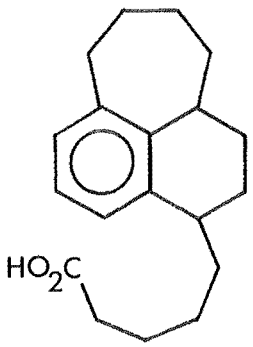
leaves an equivalent amount of monoketone **58** in the reaction mixture, and an excessive amount produces the more highly reduced hydrocarbon **59** .

The Attempted Synthesis of *1,2,3,4,8,9,10,11-Octahydro-7H-cyclohepta[ij]cyclooöcta[de]naphthalene* **60**

Two routes to this hydrocarbon appeared to be possible. The first involved the synthesis of the acid **61** which could then have been cyclized in the same manner that the acids **29** and **43a** were. The synthesis of **61** would have required a two-carbon extension of the chain of **43a** or a one-carbon extension of the chain of **29** . The former could have been achieved by the reduction of the carboxylic acid function of **43a** to its alcohol, and replacement of the hydroxy group with bromine using phosphorus tribromide. On reaction of the propyl bromide with diethyl malonate followed by hydrolysis and decarboxylation of the diester, the acid **61** would be obtained.

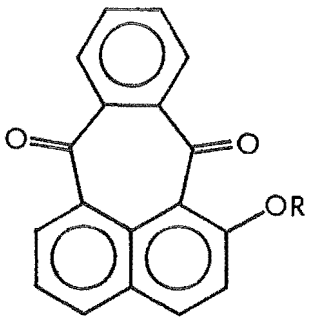


60

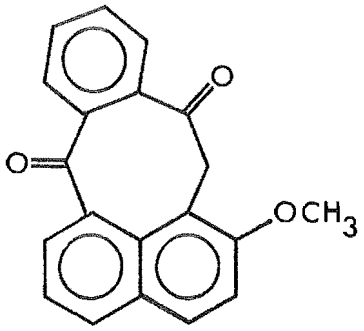


61

For the preparation of **61** via the acid **29** the steps would have involved reduction to the alcohol, conversion to the bromide, Grignard formation and carbonation. Alternatively, the acid could have been obtained by nitrile formation and its subsequent hydrolysis. None of these proposed routes, although well known, are high yielding. Considering as well the effort spent in preparing the precursors **29** and **43a** , these methods were not attempted. Instead, the possibility of forming an eight-membered ring in one step from the action of diazomethane on the ketone **30** was investigated. As a guide for this reaction we had the work of Cram and Helgeson[79] who ring expanded paracyclophanes in reasonable yield, and that of Fieser[80] and later Crombie[81] who expanded **62a** to **63** .



62a R=H
b R=CH_3



63

The ketone **30** was reacted with a large excess of diazomethane using boron trifluoride etherate as a catalyst. House observed that boron trifluoride etherate not only

catalyses ring expansion but it also inhibits epoxide formation[82], which is the main side-reaction. However, despite the catalyst and variations in reaction conditions, no ring-expanded product was detected and the starting material was recovered. A ring expansion was also attempted on the diketone **56** , a compound of similar structure to **62a**. Again, no product containing an expanded ring was detected. This is in agreement with Fieser's observations that while the compound **62a** will undergo ring expansion its methyl ether **62b** will not. It is possible that the proton of the hydroxyl group *ortho* to the carbonyl function is providing some form of intramolecular catalysis in the example of the successful reaction via **62a** .

The Attempted Fluorination of α-Substituted Carbocyclic Aromatics

The literature contains no examples of the fluorination of a carbon α to both an aromatic nucleus and a saturated carbon. There are examples of the fluorination of benzylic carbons by halide exchange[23,83], so these were attempted. For a test substrate, 1-bromoacenaphthene was chosen. This is readily obtained in a pure, crystalline form by the free radical bromination of acenaphthene using N-bromosuccinimide[84]. However, it decomposes with time with the elimination of hydrogen bromide to form acenaphthylene, and it was replaced by 1-bromo-1-phenylethane

which was more stable.

For halide exchange, three different reaction media were used: mercuric oxide and anhydrous hydrogen fluoride, from which is generated mercuric fluoride; silver (I) fluoride in acetonitrile; and anhydrous potassium fluoride in N-methylpyrrolidone. The mercuric fluoride was the first reagent used, because it appeared to be the most reactive of its type, and was reactive at low temperatures. The use of silver fluoride was motivated by its success in fluorinating complex cyclic compounds, and that of potassium fluoride by its success in fluorinating terminal benzylic carbons. These methods, unfortunately, were all fruitless on our system, and a more modern technique was turned to.

Sulphur tetrafluoride has been shown to be an excellent reagent for replacing the oxygen of a carbonyl group with two fluorine atoms[25,85]. We had cyclic ketones (e.g., 1-oxo-1,2,3,4,4a,5,6,6a,7,8,9,10-dodecahydrodicyclohepta[*de*,*ij*]naphthalene **30**) suitable for the formation of naphthylic difluoro compounds. Geminal difluoro substitution of this type has been used for the conformational analysis of decalins[86] and cyclohexanes[87]. It was difficult to deduce from the literature optimum conditions for the reaction of our system. For example, benzophenone would not react with sulphur tetrafluoride even at elevated temperatures. However, when a catalytic amount of boron trifluoride was added the reaction temperature had to be

moderated to prevent charring. On the other hand, with cyclohexanone and sulphur tetrafluoride alone charring occurred at 50°. At 39° the reaction proceeded satisfactorily[25]. When an excess of sulphur tetrafluoride was used the fluorination of a cyclic steroidal ketone occurred at 20°[88]. From these results it was concluded that while activation might be required in order to bring about the reaction of an aromatic ketone the over-riding factor was that the reaction conditions must be moderated in order to prevent charring. Reactions were therefore carried out at low temperatures (except for one at 150°) with variations in catalyst and the duration of the reaction. However, no reaction was successful, for even at 45° charring occurred, while at 20° only unreacted starting material was recovered.

The Nitro-acetoxylation of Carbocyclic Aromatics

The nitro-acetoxylation of substituted aromatic compounds in the presence of nitric acid and acetic anhydride produced very labile adducts, which were prone to undergo further reaction both in the reaction medium and during work-up.

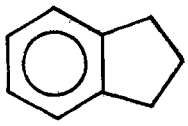
The nitro-acetoxylating reagent was prepared by mixing fuming nitric acid and acetic anhydride. In order to form acetyl nitrate nitric acid was added slowly to acetic anhydride at 0°. Acetyl nitrate does not form

below -15°[89], and decomposes at ambient temperatures or above. The addition reaction is exothermic and in order to carry out the reaction below a specified temperature the reagent was added slowly at a still lower temperature, or more efficiently, by cooling both substrate and reagent to -78°, mixing them, and then allowing the mixture to warm to the reaction temperature. The optimum reaction temperature was the lowest temperature at which the substrate would react. This is because it was found that the lower the reaction temperature the higher the proportion of dienes in the product. The lowest temperature at which a substrate would react was difficult to predetermine. Tetralin required 8 hours at 0° in order to react completely, whereas the reaction of indane was complete after only 1.5 hours at -35°, or after standing overnight at -78° with dichloromethane as solvent. This latter result indicates that indane is highly reactive towards acetyl nitrate because it was found that solvents other than acetic anhydride had a marked inhibitory effect on the reaction.

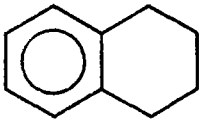
The extraction of the products was carried out by one of two methods, depending on how stable the adducts were. Moderately stable dienes were extracted by quenching the reaction mixture in halocarbon solvent (c.a. 20 mls. of solvent for 1 g. of product), washing out acids and anhydride, and evaporating the solvent. The acids and anhydride

may be extracted by extensive washings with water, but this was tedious. A more efficient method was that of washing with water to extract acids and then with dilute solutions of ammonia to extract anhydride. It was found that care had to be taken not to wash past neutrality with the aqueous ammonia, or else decomposition of the diene resulted. Highly unstable diene intermediates were quenched *in situ* at -78° by condensing gaseous ammonia directly into the reaction mixture[90]. The excess ammonia was then pumped off and the neutral residue taken up in solvent and water at room temperature and washed free of ammonium acetate. It was in this manner that the highly reactive adduct of 5,6,7,8-tetrahydrocyclohepta[*fg*]acenaphthene was isolated. After quenching, the product was dissolved in a solvent, usually CCl_4, and washed with water. The solvent was evaporated efficiently at room temperature without decomposition of diene by pumping ice water, or better, methanol from a bath cooled by dry ice, through the condenser of the evaporator.

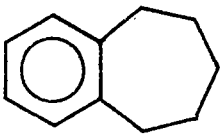
The separation of the diene adducts from the unreacted hydrocarbon and from other reaction products (usually nitro compounds) was a major problem. Only a few of the diene adducts crystallised preferentially, and because of their thermal lability the only other technique open to us was solid-liquid chromatography. Blackstock



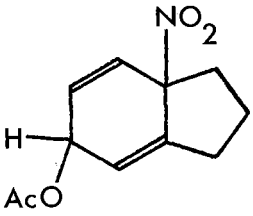
64



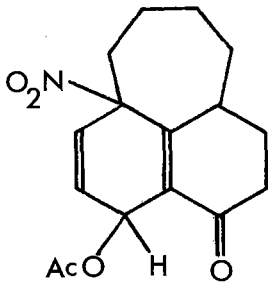
65



66

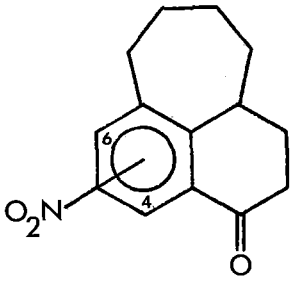


67



68 *trans*

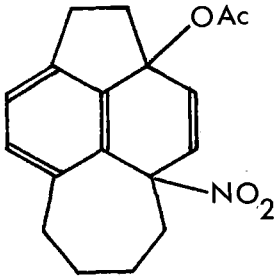
69 *cis*



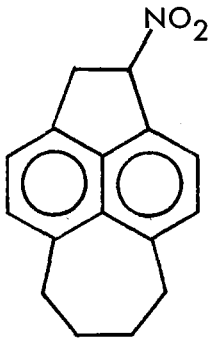
70 4-NITRO

71 5-NITRO

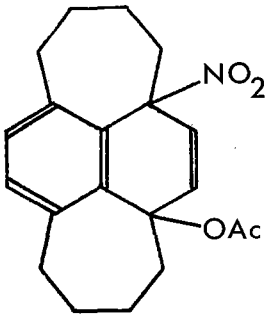
72 6-NITRO



73



74



75

could only reclaim minor amounts of diene using standard column chromatography procedures. He found that one diene decomposed more readily than the other on the column[58]. When the products were placed on a column as a 10% solution in 1:9 ether-pentane and elution was carried out rapidly by reducing the pressure at the bottom of the column[90] up to 60% of diene was recovered, but the total decomposition of one isomer still occurred. This technique was perfected when the chromatography column was fitted with a cooling jacket and the chromatography was carried out at -40° or lower, in which case quantitative reclamation of the diene was achieved. The extent of decomposition of the diene depended on the activity of the alumina. Wilkinson[91] found that at room temperature the adduct of *o*-xylene was decomposed insignificantly by 20% deactivated alumina, considerably by 10% deactivated alumina, and completely, along with acetoxy cleavage, with undeactivated alumina. He also found that the activity of the alumina had a more profound effect on the decomposition of the diene than its pH.

In this work the compounds indan (**64**), tetralin (**65**), benzsuberan (**66**), 3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**), 5,6,7,8-tetrahydrocyclohepta[*fg*]acenaphthene (**57**) and 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de,ij*]naphthalene (**17**) were reacted

with mixtures of nitric acid and acetic anhydride under various conditions, and where possible their products were isolated and characterised. A diene of the structure **67** was isolated from the reaction of indan, and a homologous compound was isolated from that of tetralin. The formation of these dienes was accompanied by the formation of a smaller amount of a second diene which from previous work[60] were assumed to be the stereoisomers of the dienes isolated. The nitro-acetoxylation of benzsuberan gave a mixture of products which were spectrally similar to those from tetralin. However, the dienes decomposed before an attempt could be made to isolate them from the reaction product. When the ketone **14** was treated with mixtures of nitric acid and acetic anhydride the stereoisomeric dienes **68** and **69** and the aromatic nitro compounds **70-72** were isolated. This is the first instance of a deactivated aromatic nucleus undergoing adduct formation of this type. When the cycloheptaacenaphthene **57** was nitro-acetoxylated the main product was the α-substituted nitro compound **74** . Only when the reaction was conducted and quenched at -78° was a diene, presumably **73** , detected. The diene of dipleiadane (**17**) was more stable, and it was detected even after its reaction mixture had been warmed to 20°. The spectral characteristics of the diene suggested it to have the structure **75** .

EXPERIMENTAL

U.v. spectra were determined on a Unicam S.P. 800 spectrometer. I.r. spectra were determined on a Perkin-Elmer model 337 spectrometer calibrated with polystyrene. N.m.r. spectra were determined on a Varian HA-60-IL spectrometer using tetramethylsilane as internal standard. Mass spectra were determined on an AEI MS-902 instrument. Microanalyses were by Dr. A. D. Campbell, University of Otago, Dunedin, New Zealand. Melting points are uncorrected.

The Synthesis of *7,8,9,10-Tetrahydrocyclohepta[de]naphthalene* (**5**)

Pleiadane (**5**) was successfully prepared via the tricyclic ketone **14** . For the preparation of the ketone **14** see scheme II.

1,2,3,7,8,9,10,10a-Octahydrocyclohepta[de]naphthalene **13**

The ketone **14** (10.0 g) was dissolved in toluene (25 mls) and refluxed for 12 hours with concentrated hydrochloric acid (150 mls), glacial acetic acid (60 mls), and zinc-mercury amalgam (25 g). The amalgam had been prepared immediately beforehand by swirling mercuric chloride (2.5 g) and powdered zinc (25 g) with dilute hydrochloric acid.

The reaction mixture was diluted with three volumes of water and the organic layer separated. The aqueous layer was washed with ether (5 x 25 mls) and the organic layers combined. These were then washed with aqueous bicarbonate solution, dried over magnesium sulphate, and concentrated. The residue was dissolved in 5 mls of benzene and columned on 30 g of alumina (Brockmann I). Elution with petroleum ether gave the hydrocarbon **13** (7.8 g, 84%); b.p. 78-80°/0.3 mm (cf 155-8°/23 mm[46]); i.r. 3065 and 3020 (aromatic C-H), 2920 and 2850 (alicyclic C-H), 1590 (aromatic ring), 1465 and 1445 (CH_2), 785, 778, 768, 746 cm^{-1}. Some unchanged tricyclic ketone (0.7 g, 7%) was recovered after elution with benzene.

7,8,9,10-Tetrahydrocyclohepta[de]naphthalene **5**

Preparation of 30% palladium-on-carbon catalyst[92]: About 5 gms of charcoal were warmed with dilute nitric acid for about one hour until fumes of nitrogen dioxide were observed. The charcoal was then filtered and washed with water and ethanol. A solution of palladium chloride dihydrate was prepared by dissolving 1 gm of the salt in 6 mls of 1N hydrochloric acid. To this was added 1.5 g of the activated charcoal and 3 mls of formalin. To the cooled mixture 6 mls of 50% potassium hydroxide were added slowly keeping the temperature below 5°. The mixture was then heated on a steam bath for 15 minutes, cooled, and

filtered. The catalyst was washed with dilute acetic acid, water, and ethanol and then dried under vacuum at 100°.

The hydrocarbon **13** (7 g) was heated at 300°, under nitrogen, with 30% palladium-on-carbon (0.4 g) for 4 hours. The product was then taken up in benzene, the catalyst filtered off, and the benzene evaporated. The residue, obtained quantitatively, was shown by v.p.c. analysis to contain the product **5** and reactant **13** in the ratio of 85:15. The desired tetrahydrocycloheptanaphthalene **5** was obtained on recrystallisation from ethanol as rhombic crystals: m.p. 54.5-55.5° (cf 55.5-57°[46]); i.r. (Nujol) 3060 and 3035 (aromatic C-H), 1595 and 1580 (aromatic ring), 832, 819, 794, 771 cm^{-1}; n.m.r. ($CDCl_3$) τ 2.7 (m, 6, aromatic CH) 6.77 (m, 4, benzylic CH_2) 7.95 p.p.m. (m, 4, alicyclic CH_2); u.v. max. (95% C_2H_5OH) 232 (ε 2140), 268 (shoulder, ε 410), 278 (ε 650), 288 (ε 780), 299 (ε 560), 308 (ε 230), 318 (ε 120), 323 nm (ε 145 m^2 mol^{-1}).

Unsuccessful attempts:

1. The condensation of diethyl succinate with dimethyl naphthalate. Dimethyl 1,8-naphthalate (**3**) (For its preparation from naphthalic anhydride see reference 93. The recrystallisation from concentrated nitric acid should not be disregarded.) (25 g) and a suspension of 50% sodium hydride (9.6 g) were refluxed in redistilled diglyme (100 mls) while diethyl succinate (8.7 g) in diglyme (25 mls)

was added dropwise over 2 hours. After refluxing for a further hour gas evolution had ceased, and the mixture was cooled to 10° C. Ethanol was then added to destroy unreacted sodium hydride, followed by ice-water (150 mls), and a slight excess of concentrated hydrochloric acid, the temperature being kept below 20° C. The organic and aqueous layers were separated and the aqueous layer was extracted with ether. The dried ether concentrate and the diglyme fraction were distilled under reduced pressure to yield an oil. I.r. studies showed no aromatic carbonyl frequencies. When a sample of the oil was refluxed for 3 hours with 10% sodium hydroxide solution naphthalic acid was isolated.

2. The Friedel Crafts condensation of naphthalene and succinic anhydride.

4-(1'-naphthyl)4-oxobutanoic acid **6a**

Naphthalene (32 g) was added over 1 hour to succinic anhydride (25 g) and aluminium chloride, which were stirred in 1,2-dichloroethane (200 mls) at 0°. After a further 4 hours the reaction vessel was removed from the ice-bath and stood at room temperature for two days. The mixture was then poured into ice-water (200 mls) and concentrated hydrochloric acid (30 mls). The solvent was removed by reduced pressure distillation. The crude acid was washed with water, dissolved in hot aqueous sodium carbonate, and

filtered. The filtrate was acidified and the resulting precipitate collected and recrystallized from glacial acetic acid. The 2'-isomer crystallized first and was filtered off. The mother liquor was diluted with three volumes of boiling water, stirred with carbon, filtered, and cooled. The crystals which formed were filtered and recrystallized from methanol to yield 4-(1'-naphthyl)4-oxobutanoic acid (**6a**) 39 g (70%); m.p. = 128-9° (cf 129-131°[94]); i.r. (Nujol) 1705 (acid C=O), 1670 cm^{-1} (aromatic C=O).

7,10-Dioxo-7,8,9,10-tetrahydrocyclohepta[de]naphthalene (**7**).

The attempted preparation of this diketone was via Friedel-Crafts condensation of methyl 4-(1'-naphthyl)4-oxobutanoate **6b** . (**6b** was prepared from its acid **6a** by refluxing it in methanol containing 5% concentrated sulphuric acid.) The conditions used were identical to those which produced 5,8-dioxo-5,6,7,8-tetrahydrocyclohepta [*fg*]acenaphthene (**56** , scheme V). The reaction was unsuccessful, only unreacted ester **6b** and its acid **6a** being recovered. In the second attempt the acid **6a** (5 g) was stirred with concentrated sulphuric acid (500 mls) for one day. The acidic solution was then stirred into four litres of ice-water and extracted with benzene (4 x 200 mls). The combined organic layers were washed with aqueous bicarbonate solution which was then acidified to yield unreacted butanoic acid. When the organic layer was dried and concentrated the

only absorption in the carbonyl region of the infrared was at 1810 cm^{-1}. When the reaction was repeated with the acid solution being heated between 40 and 50°, 8 g of product having no infrared absorption in the carbonyl region was obtained.

3. The preparation of *4-phenyloctandioc acid* (**11**) and its attempted simultaneous closure to form *3,7-dioxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de]naphthalene* (**12**).

5-Oxo-5-phenylpentanoic acid (**8a**)

Aluminium chloride (107 g, 0.8 moles) was suspended in benzene (200 mls) and stirred on an ice-bath. Glutaric anhydride (43.5 g, 0.38 moles) in benzene (100 mls) was added dropwise over 2 hours. The reaction mixture was stood at 0° for a further 30 minutes, followed by 30 minutes at room temperature before being poured into a litre of ice-cold 20% concentrated hydrochloric acid. After stirring the two phases thoroughly some undissolved solid was filtered off and the filtrate was separated into its aqueous and organic layers. The aqueous layer was extracted with ether (3 x 100 mls), which was then combined with the organic layer and washed with water before being extracted with 10% sodium hydroxide. The precipitate from the first acidification was dissolved in these alkaline washings and then washed with ether. After warming to drive off dissolved

ether the alkaline solution was cooled and acidified with 6N hydrochloric acid to yield light orange crystals of the acid **8a** : 36.5 g (50%); m.p. = 124-5° (cf 125-6°[95]); i.r. (Nujol) 1705 (acid C=O), 1680 cm^{-1} (aromatic C=O).

Ethyl 5-oxo-5-phenylpentanoate (**8b**).

The pentanoic acid **8a** was refluxed in ethanol (300 mls) with concentrated sulphuric acid (3 mls) for 4 hours. After cooling, the reaction mixture was poured into 300 mls of water and extracted with ether which in turn was extracted with saturated bicarbonate solution, saturated sodium chloride solution, and water. After drying over magnesium sulphate the solvent was removed to yield 14.0 g (61%) of the ester **8b** as an oil: i.r. (film) 1735 (ester C-O), 1680 cm^{-1} (aromatic C=O). Acidification of the bicarbonate washings yielded 6.4 g (32%) of starting material.

3,7-Dicarbethoxy-4-phenyl-hept-3-enoic acid (**9**)[96].

The pentanoate **8b** (14.0 g, 0.064 moles) in t-butanol was added to a solution of diethyl succinate (30 g, 0.17 moles) and potassium t-butoxide which had been prepared by stirring shavings of potassium (4.6 g, 0.12 moles) with dry t-butanol (40 mls) for about 2 hours under an atmosphere of nitrogen. The mixture was stirred for 20 minutes and then stood for 12 hours at room temperature. By that time it had a deep red coloration. It was then added to 100 mls

of 15% aqueous concentrated hydrochloric acid solution, and the alcohols evaporated. The yellow oily residue was taken up in ether and extracted with saturated bicarbonate solution, which when acidified was extracted with ether. The organic layer was washed with water and saturated salt solution, dried over magnesium sulphate, and concentrated to yield 13.05 g (59%) of the diester-acid **9** as a viscous oil: i.r. (film) 1735 (ester C=O), 1720 (conjugated ester C=O), 1705 (acid C=O) cm^{-1}.

4-Phenyloctandioc acid (**11**).

The dicarbethoxyheptenoic acid **9** (13.05 g) was refluxed for 4 hours with glacial acetic acid (90 mls), concentrated hydrochloric acid (45 mls), and water (65 mls). The acids were then concentrated by reduced pressure distillation and the product extracted with ether-benzene (4 x 100 mls). The organic layer was then extracted thoroughly with saturated bicarbonate solution which was washed with ether before being acidified and extracted with benzene-ether. After washing with water and drying over magnesium sulphate the organic layer was concentrated to yield 8.5 g of the olefinic diacid **10** as a gum: i.r. (film) 1705 cm^{-1} (acid C=O). The acid **10** was then dissolved in ethyl acetate and shaken overnight with 0.5 g of 5% palladium-on-carbon at a pressure of 1,000 psi of hydrogen. The catalyst was filtered off and the solvent

evaporated to give the desired acid in a quantitative yield: i.r. (Nujol) 2700-2500 (acid O-H), 1705 cm^{-1} (acid C=O). A proportionately small analytical sample of what was thought to be the diacid was obtained by recrystallizing the sodium salt of the crude reaction product. The properties of this sample were found to be compatible with those expected for

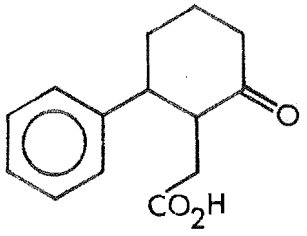
2-oxo-6-phenylcyclohexylacetic acid **76**: sublimed 125°/0.002 mm; m.p. 129-131°; i.r. (Nujol) 2700-2500 (acid O-H), 1710 (cyclic C=O), 1705 (acid C=O), 754 and 696 cm^{-1} (aromatic C-H bending); u.v. max. (95% C_2H_5OH) 211 nm (ε 760 m^2 mol^{-1}); n.m.r. ($CDCl_3$) τ 2.76 (s, 5, C_6H_5), 7.0 (m, 1, C_6H_5CH, 7.1-7.6 (m, 3, $CHCOCH_2$), 7.6-9.0 p.p.m. (m, 6, CH_2CO_2H, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 233 (25), 232.109 (87, $M_r(^{12}C_{14}{}^{1}H_{16}{}^{16}O_3)$ = 232.110), 215 (37), 214 (82), 204 (24), 189 (8), 186 (58), 174 (97), 173 (100), 172 (96), 162 (23), 158 (72), 155 (44), 145 (62), 144 (98), 143 (79), 141 (50), 131 (97), 130 (87), 129 (95), 128 (94), 127 (55), 118 (94), 117 (99), 116 (95), 115 (98), 83 (23), 55 (26).

Anal. Calcd. for $C_{14}H_{16}O_3$: C, 72.39; H, 6.94. Found: C, 72.47; H, 6.93.

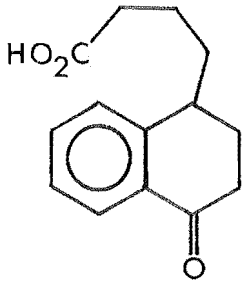
The 2,4-dinitrophenylhydrazone of **76** was prepared: m.p. 237-8°; u.v. max. (95% C_2H_5OH) 212 (ε 1870), 230 (ε 1820), 270 (shoulder, ε 1140), 365 nm (ε 2420 m^2 mol^{-1}).

Attempted synthesis of *3,7-dioxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de]naphthalene* (**12**)

The crude octandioc acid **11** (2.0 g) was added to 48.8 g of polyphosphoric acid which had been prepared by heating 25 g of phosphorus pentoxide and 23.8 g of orthophosphoric acid in a steam bath for 2 hours. The reaction mixture was swirled occasionally during a 2 hour period at 95° and was then dissipated by pouring it into 200 mls of ice-water. The product was extracted with benzene which was then washed with 10% aqueous sodium hydroxide and dried. The organic layer concentrated to a negligible amount of material, whereas the basic extraction liquor after acidification and extraction with benzene yielded 1.6 g of product which was probably 4-(4'-oxo-1',2',3',4'-tetrahydro-1'-naphthalenyl)butanoic acid (**77**): i.r. (smear) 1705 (acid C=O), 1680 cm^{-1} (aromatic C=O).



76



77

The Synthesis of *1,2,3,4,7,8,9,10-Octahydrodicyclohepta-[de,ij]naphthalene* (**17**).

Cinnamylidene acetic acid (**20**)

Freshly distilled cinnamaldehyde (**18** , 1 Kg) acetone (3 l), 10% sodium hydroxide solution (2 l), and water (30 l) were stirred for 24 hours in a large plastic garbage container. The resulting bright yellow crystalline cinnamylidene acetone (**19**) was filtered off under reduced pressure and washed with water (4 x 750 mls). The moist cake was dissolved in methanol (5 l) at 40-50° and the methanolic solution was poured with stirring into 12 litres of a solution of sodium hypochlorite which had been prepared by dissolving sodium hydroxide (1.5 Kg) in water (4 l), adding ice (10 Kg), bubbling in chlorine (1,080 gm), and making the solution up to 24 l with water. The other half of the hypochlorite solution was added in six equal portions at five minute intervals when the reaction solution had reached its maximum temperature (about 45°). Stirring of the solution was continued overnight. Excess chlorine was removed from the solution by bubbling a few grams of sulphur dioxide through it until a sample, after acidification with hydrochloric acid, gave no reaction with starch-iodide paper. The solution was then acidified with hydrochloric acid and the product which precipitated was filtered and washed with water (4 x 1250 ml). The product acid was dried and purified

by dissolving it in acetone, separating off the aqueous layer, and reducing the volume of acetone. After two recrystallizations, cinnamylidene acetic acid (**20**) was obtained as light yellow crystals: 1046 g (80%); m.p. 170-2° (cf 161-3°[98]). The dark mother liquors were discarded.

5-Phenylpentanoic acid (δ-phenylvaleric acid, **21** *)*

This acid was prepared by the catalytic reduction of cinnamylidene acetic acid (**20**) using palladium-on-carbon, and less successfully using Raney nickel.

(a) Using palladium-on-carbon: This catalyst was used at both high and low pressures. In a typical run at high pressure cinnamylidene acetic acid (40 g) was dissolved with warming in A.R. acetone (180 mls) and the solution transferred to a 250 ml hydrogenating vessel containing commercial 5% palladium-on-carbon (2 g). The mixture was then shaken at 1000 lbs. p.s.i. of hydrogen at room temperature for 4 hours. The catalyst was filtered off and the solvent evaporated to yield crystals of 5-phenylpentanoic acid (**21**): 37.7 g (92%), m.p. 53-4°. Recrystallization from 1:19 benzene-ligroin (2x) raised the m.p. to 58-9° (cf 59°[98]).

While the high pressure hydrogenation was efficient for small quantities, it was tediously repetitive for a large-scale preparation. Hence low pressure hydrogenation

was attempted and it was found to be successful. In the final run, cinnamylidene acetic acid (600 g) was dissolved in A.R. acetone (5 l) in a 10-litre Buchner flask mounted on a stirrer-hot plate. The Buchner flask was fitted in series with a gas bubbler, so that hydrogen uptake could be observed, and a low pressure gauge. After addition of 5% palladium-on-carbon (20 g) the vessel was flushed with nitrogen and hydrogen and then filled with hydrogen to a pressure of 30 lbs. p.s.i. The mixture was warmed and stirred for four days, after which time the uptake of hydrogen had ceased. To check that this was not due to the catalyst being poisoned the reaction vessel was flushed with nitrogen (the catalyst ignites spontaneously in mixtures of hydrogen and oxygen) and an additional 5 g of catalyst was added. When the vessel was recharged with hydrogen no further gas uptake was observed. The catalyst was filtered off and the acetone evaporated. The residue was recrystallized from 1:19 benzene-ligroin (2x) to yield 5-phenyl-pentanoic acid (**21**): 439 g (71%); m.p. 58-9° (cf 59°[98]); b.p. 140-2°/14 mm (cf 190-3°/30 mm[1]).

The recrystallization mother liquors were distilled to yield 6-phenylhexan-2-one: 135 g (22%); b.p. 110-130°/14 mm.

(b) Using Raney nickel: The *in situ* activation of the catalyst was conducted as specified by Anderson and

Wang[66], but the overall yield from cinnamaldehyde was only 11% (cf 95%[66]). For *ex situ* activation W_5 Raney nickel was prepared by the method of Adkins and Billica[99]. Plati *et al* stated[97] that cinnamylidene acetic acid was "catalytically hydrogenated at 110° in ethanol using Raney nickel (half-hour)". However, only after variations of the quantity of catalyst, alkalinity, pressure, and the duration was any reaction seen. Cinnamylidene acetic acid (10 g) was shaken with sodium hydroxide (2 g) and the catalyst (20 g) in ethanol (150 mls) for seven hours at 110° and 900 lbs. p.s.i. to yield 5-phenylpentanoic acid: 2.0 g (20%); m.p. 53-4°. Only traces of the starting material were recovered.

Benzsuberone (**22**).

Polyphosphoric acid required for the preparation of benzsuberone from 5-phenylpentanoic acid (**21**) was prepared by dissolving phosphorus pentoxide (1.5 Kg) in 95% orthophosphoric acid (1430 g, 780 ml) in a 3-litre round-bottomed flask. It was necessary to moderate the heat of mixing by immersing the flask in ice water. The dissolution of the phosphorus pentoxide was encouraged by mechanically stirring the mixture at 95° for two hours. To this mixture was then added 5-phenylpentanoic acid (100 g) and the stirring was continued for a further 10 minutes. The stirrer was then removed and replaced by a drying tube. The flask was maintained at 95° with occasional swirlings for two hours before

the syrupy mixture was dissipated by pouring it into three litres of ice water. The products were extracted with benzene (4 x 250 mls) (the use of a heavier-than-water solvent such as chloroform is of no advantage as the aqueous acid is still very dense) which in turn was extracted with 5% aqueous hydroxide. The combined benzene layers were concentrated and distilled to give benzsuberone: 80.9 g (90%); b.p. 101-2°/2 mm (cf 124-5°/7 mm[1]).

3-Carbethoxy-3-(1',2'-benzocyclohepta-1',3'-dien-3'-yl) propionic acid (**23a**) and *1',2'-benzocyclohepta-1',3'-dien-3'-ylbutandioic acid* (**23b**)

Benzosuberone (160 g, 1.0 moles) and diethyl succinate (261 g, 1.5 moles) were added to a solution of potassium t-butoxide, prepared from potassium (43 g, 1.1 moles) and t-butyl alcohol (1.2 litres), under nitrogen. The solution was heated under reflux for 40 minutes and then allowed to stand at room temperature for 24 hours. The mixture was acidified with hydrochloric acid, the solvent removed and the residue taken up in ether. After washing with water, the product half-ester was extracted into bicarbonate and the bicarbonate solution washed with ether. The product was extracted back into ether from the acidified bicarbonate solution and the ether removed yielding the carbethoxybenzocycloheptadienylpropanioc acid **23a**[69], presumably contaminated with the *exo* isomer, as a clear oil

(261 g, 90%): i.r. 1740 (ester C=O), 1710 cm^{-1} (acid C=O); n.m.r. (CCl_4) τ 2.85 (m, 4, C_6H_4), 5.95 (t, 0.6, C*H*=C). Benzosuberone (13 g, 8%) was recovered.

The carbethoxypropanoic acid **23a** (2 g) dissolved in methanol (50 g) and water (50 ml) containing potassium hydroxide (50 g) was stirred at room temperature for 10 days. The solution was acidified with hydrochloric acid and the diacid was extracted with dichloromethane. After treating the extract with norite the solvent was removed and the residue was recrystallized from aqueous methanol and then sublimed. The sublimate, which melted and re-solidified at about 70° and then remelted at 159-161°, was recrystallized from benzene containing a little methanol to give 1',2'-benzocyclohepta-1',3'-dien-3'-ylbutandioic acid: m.p. 159-159.5°; i.r.(KBr) 1710 (shoulder), 1700 cm^{-1} (acid C=O); n.m.r. ($CDCl_3$) τ -1.75 (s, 2, CO_2H), 2.72 (m, 4, C_6H_4), 3.8 (t, 1, C*H*=C), 5.96 (m, 1, C=C-C(*H*)CO_2H), 7.05 (m, 2, $C_6H_4CH_2$), 7.5 (m, 2, CH_2CO_2H), 7.8 (m, 2, C=CH-CH_2), 8.16 (m, 2, $CH_2CH_2CH_2$); mass spectrum (70 eV) *m/e* (relative intensity) 260.1046 (27, M_r ($^{12}C_{15}{}^{1}H_{16}{}^{16}O_4$) = 260.1049), 242.0942 (28, $C_{15}H_{14}O_3$), 214 (23), 201 (38), 155 (47), 143 (100), 141 (42).

Anal. Calcd. for $C_{15}H_{16}O_4$: C, 69.21; H, 6.20. Found: C, 69.16; H, 6.29.

3-(1',2'-Benzocyclohepta-1',3'-dien-3'-yl)propanoic acid (**24**) *and the lactone of 3-(1',2'-Benzo-3'-hydroxycyclohepta-1'-en-3'-yl)propanoic acid* (**25**)

The carbethoxypropanoic acid **23** (516 g, 1.79 moles) was heated under reflux for 48 hours in a solution of acetic acid (3 litres), hydrochloric acid (1.5 litres) and water (2.2 litres)[70]. The mixture was concentrated by distillation under reduced pressure and the acid taken up in benzene. The benzene solution was washed with water and the acid was extracted with saturated carbonate solution which was in turn extracted with dichloromethane and the dichloromethane and benzene solutions were then combined. The carbonate solution was acidified and the liberated acid extracted with dichloromethane. The solution was dried, the solvent removed and the residue recrystallized from 5% benzene-ligroin to yield the unsaturated acid **24a** (98 g, 25%): m.p. 71.5-72°; i.r. (Nujol) 1705 cm^{-1} (acid C=O); n.m.r. (CCl_4) τ -1.83 (s, 1, CO_2H), 2.89 (m, 4, C_6H_4), 4.03 (t, 1, C*H*=C), 7.0 - 8.2 p.p.m. (m, 10); mass spectrum (70 eV) *m/e* (relative intensity) 216.1124 (40, M_r ($^{12}C_{14}{}^{1}H_{16}{}^{16}O_2$) = 216.1152), 156 (31), 143 (100), 141 (43), 115.0546 (43, C_9H_7).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.60; H, 7.52.

A residual acidic oil (171 g) was also obtained.

The combined benzene-dichloromethane neutral solution was dried, the solvent removed and the residue recrystallized from 5% benzene-ligroin to yield the lactone **25** (79 g, 21%): m.p. 132-132.5° (cf 134°[100]); i.r. (Nujol) 1775 cm^{-1} (lactone C=O); n.m.r. ($CDCl_3$) τ 2.83 (m, 4, C_6H_4), 7.13 (m, 2, CHC_6H_4), 7.53 (s, 4), 7.93 (m, 6); mass spectrum (70 eV) *m/e* (relative intensity) 216.1161 (100, M_r ($^{12}C_{14}{}^{1}H_{16}{}^{16}O_2$) = 216.1161), 187.0737 (15, $C_{12}H_{11}O_2$), 161.0972 (50, $C_{11}H_{13}O$), 143.0861 (59, $C_{11}H_{11}$), 141 (9).

Anal. Calcd. for $C_{14}H_{16}O_2$: C, 77.75; H, 7.46. Found: C, 77.73, 7.47.

A residual fraction (53 g) was obtained which was combined with the residual acid fraction and re-hydrolysed for 5 days and the olefinic acid **24** and the lactone **25** isolated as described above. The residues were subjected to a third hydrolysis and at this stage the total yield was 84% consisting of acid and lactone in the ratio of 4:3.

3-(1',2'-Benzocyclohept-1'-en-3'-yl)propanoic acid **26**

(a) From the benzocycloheptadienylpropanoic acid **24** . The acid (28.3 g, 0.13 moles) was dissolved in acetone (150 ml) and hydrogenated over 5% palladium-on-carbon (2 g) in a shaking autoclave at 8 MN m^{-2} for 4 hours. The catalyst was filtered off and the solvent removed under reduced pressure to give the benzocycloheptenylpropanoic acid **26** (25.8 g, 90.5%) as a clear oil.

(b) From the lactone **25**. The lactone (79 g, 0.37 moles) was heated under reflux for 6 hours in acetic acid (1 litres) with red phosphorus (60 g, 1.9 moles), iodine (20 g, 0.16 moles) and water (20 ml)[101]. The phosphorus was filtered off, the solution concentrated by distillation under reduced pressure and poured into 5% sodium bisulphite solution (2 litres). The organic layer was taken up in benzene-ether and the acid extracted with saturated sodium carbonate solution which was then acidified and extracted with dichloromethane. The dichloromethane solution was dried and the solvent removed yielding the benzocycloheptenylpropanoic acid **26** (66 g, 82%). The residual benzene-ether solution was dried and the solvent removed to leave unreacted lactone **25** (12 g, 16%).

The acid **26** was distilled under reduced pressure and recrystallized from methanol: b.p. 164-8°/0.7 mm (cf 140-7°/0.3 mm[44]); m.p. 52.5-53.5°; i.r. 1705 cm^{-1} (acid C=O); n.m.r. (CCl_4) τ -1.98 (s, 1, CO_2H), 3.03 (m, 4, C_6H_4), 7.20 (m, 3, $CH_2C_6H_4CH$), 7.74 (m, 4), 8.24 p.p.m. (m, 6); mass spectrum (70 eV) *m/e* (relative intensity) 218.1310 (100, M_r ($^{12}C_{14}{}^{1}H_{18}{}^{16}O_2$) = 218.1307), 200 (2), 158.1080 (29, $C_{12}H_{14}$), 145.1012 (100, $C_{11}H_{13}$), 143.0852 (26, $C_{11}H_{11}$), 129.0694 (28, $C_{10}H_9$), 117.0698 (27, C_9H_9), 115.0545 (36, C_9H_7), 91.0530 (C_7H_7).

Anal. Calcd. for $C_{14}H_{18}O_2$: C, 77.03; H, 8.31. Found: C, 77.06; H, 8.37.

The isolation and characterisation of the products obtained as a neutral fraction after the reduction of crude samples of the lactone **25** .

One sample of neutral compounds obtained after the red phosphorus-iodine reduction was shown by v.p.c. analysis on a 5' SE30 column at 200° to contain five compounds with retention times of 1.3 (6%), 2.0 (14%), 3.0 (35%), 4.6 (42%), and 6.5 minutes (3%). These compounds were separated to some extent by column chromatography: 27 g were placed on 200 g (28 x 330 mm) of basic alumina (activity I) and eluted with 400 mls each of petroleum ether, 1:19 benzene-petroleum ether, benzene, and ether. The petroleum ether eluate contained 300 mgm of the compounds having retention times of 2.0 and 3.0 minutes. These were recolumned on 30 g (15 x 180 mm) of basic alumina (activity I) and eluted with 75 mls each of pentane (3 x), 1:19 benzene-pentane, and benzene. The benzene-pentane eluate concentrated to 90 mgm which comprised more than 99% of the compound with the retention time of 3.0 minutes. It was recrystallized from methanol and found to be

1,2,3,4-tetrahydrophenanthrene (**36**): m.p. 27.9-28.5° (cf 33-34°[102]), i.r. (melt) 3060 (aromatic C-H), 2945, 2870, 2850 (aliphatic C-H), 1600, 1520, 1435, 1390 (aromatic ring), 830, 800, 763, 738 (aromatic C-H bending); u.v. max. (95% C_2H_5OH) 233 (ε 2350), 264 (ε 575), 273.5

(ε 690), 279.5 (ε 730), 283 (ε 685), 291 (ε 550), 307.5 (ε 135), 313.5 (ε 90), 321.5 nm (ε 130 m^2 mol^{-1}); n.m.r. (CCl_4) τ 2.0-3.1 (m, 6, $C_{10}H_6$), 7.1 (m, 4, $C_{10}H_6CH_2$), 8.1 p.p.m. (m, 4, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 182 (100, M_r ($^{12}C_{14}{}^{1}H_{14}$) = 182), 167 (14), 165 (18), 155 (55), 154 (19), 153 (14), 141 (25).

The tetrahydrophenanthrene was further characterised by treating a mixture of the tetrahydro and octahydro compounds **36** and **38** (100 mgm) with 30% Pd/C for 8 hours at 300°. The product was taken up in benzene and the catalyst was filtered off. The concentrated benzene solution was placed on 30 g (15 x 180 mm) of basic alumina (activity I) and eluted with 150 mls each of pentane, 1:9 benzene-pentane, and benzene. The concentrate of the benzene eluate (0.06 g) was yellow and mass spectra suggested that it contained dimers: *m/e* (relative intensity) 364 (18), 362 (9), 360 (22), 258 (14), 179 (20), 178 (100), 176 (18). The benzene-pentane elutate concentrated to a white solid (0.03 g) which was sublimed: m.p. 91-4°. A mixture of this sample and an authentic sample of *phenanthrene* (m.p. 98-100°) melted at 95-98°. The two samples also had identical i.r., n.m.r., and mass spectra.

The second pentane eluate concentrated to 80 mgm and was shown by v.p.c. to contain the compounds with retention times of 2.0 and 3.0 minutes in the ratio 9:1.

The major component of the mixtures could not be purified by crystallization, but its spectral properties in consultation with those of tetrahydrophenanthrene **36** suggested that the compound with a retention time of 2 0 minutes was

1,2,3,4,4a,9,10,10a-Octahydrophenanthrene (**38**): i.r. (film) 3070, 3025 (aromatic C-H), 2935, 2860 (aliphatic C-H), 1600, 1490 (aromatic ring), 1450 (aliphatic C-H bending), 753, 730 cm^{-1} (aromatic C-H bending); u.v. max. (95% C_2H_5OH) 204 (ε 860), 220 nm (ε 1060 m^2 mol^{-1}); n.m.r. (CCl_4) τ 3.08 (s, 4, C_6H_4), 7.0-7.4 (m, 3, $CHC_6H_4CH_2$), 8.0-8.7 p.p.m. (m, 11, alicyclic CH and CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 186 (100, M_r ($^{12}C_{14}{}^{1}H_{18}$) = 186), 158 (22), 143 (66), 129 (67), 117 (25), 104 (35).

The final (ether) eluate of the original column concentrated to 4.5 g of an oil which partially crystallized and which v.p.c. indicated to contain three compounds with retention times of 1.3 minutes (5%), 4.6 minutes (85%), and 6.5 minutes (10%). Further column chromatography separated the compounds into fractions of the first pair and second pair, but no compound was isolated by itself. The component with the retention time of 4.6 minutes was isolated via its bisulphite adduct and purified by column chromatography. The compound liberated from the adduct (0.79 g) was columned on 40 g (14 x 440 mm) of basic alumina (3% aqueous deactivation) and eluted with pentane and benzene.

The first two benzene fractions concentrated to 0.53 g of a clear viscous oil which was crystallized (2x) from pentane to give

1,2,3,4,4a,9,10,10a-Octahydro-4-oxophenanthrene (**37**): m.p. 41.1-42.0° (cf 39-40°[103]); i.r. (melt) 3075, 3030 (aromatic C-H), 2950, 2875 (aliphatic C-H), 1710 (alicyclic C=O), 1605, 1495 (aromatic ring), 1450 (aliphatic C-H bending), 763, 742 cm^{-1} (aromatic C-H bending); u.v. max. (95% C_2H_5OH) 201 (ε 620), 219 nm (shoulder, ε 260 m^2 mol^{-1}); n.m.r. (CCl_4) τ 3.0 (m, 4, C_6H_4), 6.9-7.4 (m, 3, $CHC_6H_4CH_2$), 7.4-7.75 (m, 3, $CHCOCH_2$), 7.75-8.7 p.p.m. (m, 6, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 200.121 (100, M_r ($^{12}C_{14}{}^{1}H_{16}{}^{16}O$) = 200.120), 199 (31), 185 (51), 182 (66), 172 (50), 171 (21), 167 (21), 157 (64), 156 (34), 154 (35), 144 (81), 143 (81), 142 (44), 141 (68), 130 (38), 129 (92), 128 (98), 127 (90), 117 (39), 116 (36), 115 (76), 91 (37), 55 (19), 42 (36).

Anal. calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05. Found: C, 83.72; H, 7.93.

The *2,4-dinitrophenylhydrazone* of **37** was prepared: m.p. 205-207°; u.v. max. (C_2H_5OH) 201 (ε 730), 220 (ε 650), 270 (shoulder, ε 330), 369 nm (ε 1020 m^2 mol^{-1}). The extinction coefficients for these peaks are probably low. The *semicarbazone* of **37** melted at 231.5-232.0° (decomp., cf 229-231°[102]).

The compound with the retention time of 1.3 minutes was not isolated by itself but was obtained as a 1:4 mixture with the oxophenanthrene **37**. A comparison of the spectra of this mixture and that of the pure oxophenanthrene suggested that the compound was unreacted benzsuberone.

3-Oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de]naphthalene (**14**).

The benzocycloheptenylpropanoic acid **26** (116 g, 0.53 moles) was heated on a steam bath, with a solution of phosphorus pentoxide (1.5 Kg) in 95% orthophosphoric acid (780 mls) for 2 hours. The mixture was poured into ice-water (3 l) and the ketone **14** extracted with benzene (4 x 250 mls). The benzene extract was washed with saturated sodium carbonate solution, dried and the solvent removed. On distillation of the residue the oxo-octahydrocycloheptanaphthalene was obtained as an oil (99.6 g, 93.5%) which was crystallized from methanol at -70°: b.p. 160-170°/1.3 mm; m.p. 59-60° (cf 43-44°[46]); i.r. 1685 cm^{-1} (aromatic C=O); n.m.r. (CCl_4) τ 2.25 and 2.89 (m, 1 and 2, C_6H_3) 7.12 (m, 3, $CH_2C_6H_3CH$), 7.55 (m, 2, CH_2CO), 8.16 p.p.m. (m, 8, $CH_2CH_2CH_2CH_2CHCH_2CH_2CO$); u.v. max. (95% C_2H_5OH) 216 (ε 1410), 253.5 (ε 1000), 300.5 nm (ε 200 m^2 mol^{-1}); mass spectrum (70 eV) *m/e* (relative intensity) 200.1204 (73, M_r ($^{12}C_{14}{}^{1}H_{16}{}^{16}O$) - 200.1201), 172 (110, 158.1109 (100, $C_{12}H_{14}$).

Anal. Calcd. for $C_{14}H_{16}O$: C, 83.96; H, 8.05

Found: C, 83.84; H, 8.21.

4,5-Benzo-1,2,3,6,7,8-hexahydro-1-oxoazulene **39**

(a) As a by-product in the formation of the ketone **14** : A sample (2.1 g) of concentrated mother liquor from the recrystallization of **14** was columned on 10 g (15 x 440 mm) of acidic alumina (activity I). Elution of the column with petroleum ether (500 mls) and benzene (500 mls) brought down 1.3 g of compound which was mainly the ketone **14** . Ether (120 mls) eluted 0.45 g of a yellow solid which was mainly the oxoazulene **39** . This was re-columned on 12 g (11 x 130 mm) of basic alumina (5% aqueous deactivation). The column was eluted with 40 mls each of pentane, 1:4 benzene-pentane, benzene, and ether. The oxo-azulene was obtained as a pale yellow solid from the con-centrate of the benzene fraction and was purified by recrystallization from pentane and sublimation to give a white solid: m.p. 58.1-58.9° (cf 60-62°[69]); i.r. (melt) 3070, 3030 (aromatic C-H), 2930, 2870 (aliphatic C-H), 1685 (conjugated C=O), 1655 (tetrasubstituted C=C), 1620, 1565, 1592 (aromatic ring), 1450, 1380 (aliphatic C-H bending), 765, 735 cm^{-1} (aromatic C-H bending); u.v. max. (95% C_2H_5OH) 200 (ε 830), 212 (ε 870), 224 (ε 1030), 230 (ε 1050), 288 nm (ε 1930 m^2mol^{-1}); n.m.r. (CCl_4) τ 2.4-3.0 (m, 4, C_6H_4), 6.9-7.3 (m, 4, $C_6H_4CH_2$, $COCH_2$), 7.4-7.7 (m, 4, $C{=}C{-}CH_2$), 7.8-8.2 p.p.m. (m, 2, alicyclic CH_2); mass

spectrum (70 eV) *m/e* (relative intensity) 198 (86, M_r ($^{12}C_{14}{}^{1}H_{14}{}^{16}O$) = 198), 183 (21), 170 (24), 166 (70), 165 (61), 142 (29), 141 (100), 128 (32), 115 (36).

The *semicarbazone* of **39** was prepared: m.p. 227-9° (cf 236°[69]).

(b) From the cyclization of the olefinic acid **24** : The olefinic acid (108 mgm) was treated with polyphosphoric acid (4.88 g: 2.5 g P_2O_5, 2.38 g orthophosphoric acid) at 95° for 2 hours. The syrupy reaction medium was dissipated with 50 mls of ice-water which was then extracted with ether-benzene (3 x 20 mls) which in turn was extracted with 5% aqueous potassium hydroxide (2 x 50 mls). The organic layer was dried over magnesium sulphate and concentrated. The concentrate was columned on 3.0 g (5 x 120 mm) of neutral alumina (5% aqueous deactivation) which was eluted with pentane and benzene. The benzene fraction concentrated to 81 mgm (82%) of the oxoazulene which was recrystallized from pentane: m.p. 57.5-58.5°. This compound had i.r., n.m.r. and mass spectral characteristics and v.p.c. retention time identical to those found for the oxoazulene **39** which was isolated as a by-product from the formation of the ketone **14** .

4-(1',2',3',7',8',9',10',10a'-Octahydrocyclohepta[de]naphthalen-3'-ylidene)but-2-enoic acid (**28a**)

The ethyl γ-bromocrotonate used in this reaction was

a sample which had previously been prepared in this department. It was redistilled: 100-105°/c.a. 14 mm (cf 105-110°/15 mm[1]). In subsequent reactions methyl γ-bromocrotonate was used. It was prepared by a hybrid method of Ziegler[104] and Hasbrouck and Speilman[105]: Recrystallised N-bromosuccinimide (N.B.S., 400 g, 2.25 moles), methyl crotonate (290 g, 2.9 moles), and benzoylperoxide (5 g) in distilled carbon tetrachloride (1 l) were slowly brought to reflux over half an hour. The solution turned orange just prior to reflux but cleared shortly afterwards. N.B.S. was barely soluble in CCl_4 and it sank to the bottom of the reaction flask whereas succinimide floated on the surface, and hence the progress of the reaction could be readily followed. N.B.S. was no longer visible at the bottom of the flask after half an hour's reflux the reaction was cooled. The succinimide was filtered off and the CCl_4 evaporated. The residue was distilled to give methyl γ-bromocrotonate 340 g (84.5% based on N.B.S.), b.p. 98-105°/c.a. 14 mm (cf 105-110°[105]).

The zinc used in this reaction was 30 mesh reagent grade which had been heated at 100° for 15 minutes with a solution of concentrated sulphuric acid and concentrated nitric acid (100 g : 50 mls : 0.5 mls). The zinc was filtered off and washed (3 x 100 mls) each with distilled water, acetone, and anhydrous ether. It was then dried overnight

under vacuum at 90°.

Ethyl γ-bromocrotonate (95 g, 0.48 moles) was added to a mixture of zinc dust (50 g) and the tricyclic ketone **14** (96 g, 0.48 moles) dissolved in benzene (250 ml) and ether (250 ml), and a crystal of iodine added to initiate the reaction. More crotonate (70 g, 0.36 moles) and zinc dust (140 g) was added over 24 hours. The mixture was stirred and heated under reflux for the initial 12 hours and stirred at room temperature for a further 48 hours. The reaction mixture was added to ice and dilute acetic acid and the aqueous and organic layers separated. The aqueous layer and the zinc remaining in the reaction flask were extracted with ether-benzene and the combined organic layers washed successively with 1% ammonia, water and saturated brine. The solution was dried and the solvent removed giving crude hydroxy ester **27** : i.r. 3505 cm^{-1} (OH). The ester was dissolved in ethanol (2 litres) and stirred overnight with 50% potassium hydroxide solution (600 ml). The solution was then diluted with water and extracted with benzene-ether which was in turn extracted with saturated sodium carbonate solution. The combined aqueous layers were acidified and extracted with benzene-ether. After removal of the solvent from the acidic extract the residue was repeatedly recrystallized from methanol to give the yellow octahydrocyclo-

heptanaphthalenylidenecrotonic acid **28a** (35 g, 26%): m.p. 215-217° (with sublimation); i.r. (Nujol) 1675 cm^{-1} (conjugated acid C=O); mass spectrum (70 eV) *m/e* (relative intensity) 268 (61, M_r ($C_{18}H_{20}O_2$) = 268), 223 (100), 167 (49).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.62; H, 7.51.

4-(1',2',3',7',8',9',10',10a'-Octahydrocyclohepta[de]naphthalen-3'-yl)butanoic acid (**29**)

In a typical reduction the diene-acid **28a** (5.1 g) was dissolved in warm acetic acid-benzene solution (150 ml) and shaken in an atmosphere of hydrogen at 5 MN m^{-2} for 4 hours. The catalyst was filtered off and the solvent evaporated. The residue was taken up in hot ligroin and filtered. The crystals which were deposited on cooling were recrystallized (x 3) yielding the octahydrocycloheptanaphthalenylbutanoic acid **29** (4.7 g, 91%): m.p. 111.5-112.5°; i.r. (Nujol) 1690 cm^{-1} (acid C=O); n.m.r. (CCl_4) τ 3.12 (m, 3, C_6H_3), 7.28 (m, 4, $CH_2C_6H_3(CH)CH$), 7.66 (m, 2, CH_2CO_2H), 8.28 p.p.m. (m, 14, alicyclic and acyclic CH_2) mass spectrum (70 eV) *m/e* (relative intensity) 272 (27, M_r ($C_{18}H_{24}O_2$) = 272), 185 (100), 143 (15).

Anal. Calcd. for $C_{18}H_{24}O_2$: C, 79.37; H, 8.88. Found: C, 79.47; H, 8.95.

1-Oxo-1,2,3,4,4a,5,6,6a,7,8,9,10-dodecahydrodicyclohepta [de,ij]naphthalene (**30**).

The acid **29** (7.1 g) was heated with a solution of phosphorus pentoxide (250 g) in 95% orthophosphoric acid (240 g) for 2 hours. The mixture was worked up as described above for the tricyclic ketone **14**. The distilled tetracyclic ketone (6.0 g, 90%) was recrystallized from pentane: b.p. 210-220°/2 mm; m.p. 73.5-74.5°; i.r. 1678 cm^{-1} (aromatic ketone C=O); n.m.r. (CCl_4) τ 2.92 (q, 2, J = 8 Hz) 6.9-7.5 p.p.m. (m, 6, $CH_2C_6H_2(CH)CH$, CH_2CO) 7.9-8.7 (m, 14, alicyclic CH_2) mass spectrum (70 eV) *m/e* (relative intensity) 254 (100, M_r ($C_{18}H_{22}O$) = 254), 236 (24), 226 (30), 198 (30), 183 (46), 141 (46).

Anal. Calcd. for $C_{18}H_{22}O$: C, 84.86; H, 8.72. Found: C, 85.05; H, 8.87.

1,2,3,4,4a,5,6,6a,7,8,9,10-Dodecahydrodicyclohepta[de,ij] naphthalene (**31**).

Zinc dust (5 g) and mercuric chloride (0.5 g) were swirled with dilute hydrochloric acid for a few minutes and the acid then decanted off. The tetracyclic ketone **30** (1.0 g) in toluene (5 mls) was added to the amalgamated zinc followed by acetic acid (30 mls) and concentrated hydrochloric acid (12 mls) and the mixture heated under reflux for 24 hours. The reaction mixture was diluted with water and extracted with ether (5 x 25 mls). The ethereal

extract was washed with saturated sodium bicarbonate solution, dried and the solvent removed. The residue was chromatographed on alumina (Brockmann 1) with petroleum ether as eluant. Benzene was used to elute a trace (0.03 g) of the ketone. The hydrocarbon **31** (0.85 g, 91%) obtained from the eluate was recrystallized from pentane: m.p. 52-52.5°; n.m.r. (CCl_4) τ 3.33 (s, 2, C_6H_2), 7.27 (m, 6, $CH_2(CH)C_6H_2(CH)CH_2$), 7.9-8.7 p.p.m. (16, alicyclic CH_2) mass spectrum (70 eV) *m/e* (relative intensity) 240 (100, M_r ($C_{18}H_{24}$) = 240), 198 (21), 183 (34).

Anal. Calcd. for $C_{18}H_{24}$: C, 89.94; H, 10.06. Found: C, 90.00; H, 10.29.

1,2,3,4,7,8,9,10-Octahydrodicyclohepta[de,ij]naphthalene (**17**)

The dodecahydro compound **31** (4.1 g) was heated under an atmosphere of nitrogen with 30% palladium-on-carbon (0.3 g) in a Claisen flask fitted with a cold finger and placed in a silicone-oil bath. Hydrogen evolution started at 260° and continued for about 4 hours as the temperature was slowly raised to 310°. At the latter temperature hydrogen evolution was minimal and heating was discontinued. Polymerisation occurred above this temperature. The products were isolated by taking the reaction mixture up in a small amount of benzene and chromatographing it through a short column (17 x 2.5 cm) of alumina using petroleum ether as eluant. Under ultraviolet light three bands were revealed. The

first fraction obtained was unreacted dodecahydro compound **31** (1.48 g, 36%), the second the desired octahydro compound **17** (2.45 g, 61%), and the third an unidentified high molecular weight compound which was eluted with benzene. The octahydrodicycloheptanaphthalene was recrystallized from pentane: m.p. 143-144°; n.m.r. (CCl_4) τ 3.15 (s, 4, aromatic C*H*) 6.90 (broad, 8, benzylic CH_2), 8.04 p.p.m. (m, 8, alicyclic CH_2); u.v. max. (95% C_2H_5OH) 217 (shoulder, ε 1540), 238.5 (ε 2160), 289 (shoulder, ε 770), 299.5 (ε 970), 311 (shoulder, ε 740), 317.5 (ε 560), 332 nm (ε 260 m^2 mol^{-1}); mass spectrum (70 eV) *m/e* (relative intensity) 236 (100, M_r) ($C_{18}H_{20}$) = 236), 221 (8), 208 (4), 207 (5), 179 (9).

Anal. Calcd. for $C_{18}H_{20}$: C, 91.47; H, 8.53. Found: C, 91.34; H, 8.75.

The Synthesis of *2,3,6,7,8,9-Hexahydro-1H-cyclohepta[gh] phenalene* (**46**)

3-Carbethoxy-3-(1',2',3',7',8',9',10',10a'-octahydrocyclohepta[de]naphthalen-3'-ylidene)propionic acid (**41b**)

3-Oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*] naphthalene (**14**) (10.0 g, 0.05 moles) and diethyl succinate (13.05 g, 0.075 moles) were added under an atmosphere of nitrogen to a slurry of potassium t-butoxide (0.055 moles) which had been prepared by stirring potassium shavings (2.15 g) with dry t-butyl alcohol until all the potassium

had dissolved. After heating under reflux for 40 minutes the solution was stood at room temperature for 24 hours before being acidified with hydrochloric acid. The solvent was removed and the residue taken up in ether. The ether solution was washed with water, the product half-ester extracted into bicarbonate and the bicarbonate solution washed.

The product was extracted back into ether from the acidified bicarbonate solution and the ethereal solution dried. After removal of the ether the half-ester **41b** (13.42 g, 82%) was obtained: i.r. 1710 cm^{-1} (conjugated ester C=O and acid C=O); n.m.r. (CCl_4) τ 0.04 (s, 1, CO_2H), 3.05 (m, 3, C_6H_3), 5.9 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$), 6.45 (m, 2, $C{=}C{-}CH_2CO_2H$), 6.7-7.7 (5, $CH_2C_6H_3CH$ and $CH_2C{=}C{-}CO_2$), 7.7-8.7 (8, alicyclic CH_2), 9.0 p.p.m. (t, J = 7 Hz, $CH_2{-}CH_3$).

Methyl 3-carbethoxy-3-(1',2',3',7',8',9',10',10a'-octahydrocyclohepta[de]naphthalen-3'-ylidene)propionate (**41c**)

The half-ester **41b** (3.4 g) was treated with excess diazomethane, allowed to stand overnight at 5° and the solvent then evaporated. The residue was taken up in petroleum ether and chromatographed on neutral alumina (100 g, Brockmann activity II), using petroleum ether as solvent. V.p.c. analyses on a 5 ft SE30 column of the crude diester showed that two compounds were present in an 80:20 ratio.

These two compounds were not separated by the column chromatography nor by subsequent distillation. It is suggested that the two compounds are geometrical isomers with the carbethoxy group being *cis* to the aromatic ring in one case and *trans* in the other. The diester **41c** had b.p. 176-178°/0.05 mm, i.r. 1740 and 1705 cm^{-1} (ester C=O); n.m.r. (CCl_4) τ 3.0 (m, 3, C_6H_3), 6.0 (q, 2, J = 7 Hz, $CO_2CH_2CH_3$), 6.35 (s, 3, CH_3O), 6.5 (m, 2, $C{=}C{-}CH_2CO_2$), 6.7-8.8 (13), 9.0 p.p.m. (t, J = 7 Hz, CH_2CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 342.1832 (20, M_r ($^{12}C_{21}{}^{1}H_{26}{}^{16}O_4$) = 342.1831), 311 (14, $C_{20}H_{23}O_3$), 310 (8), 298 (9), 297 (60), 296 (100), 282 (13), 268 (99), 264 (40).

Anal. Calcd. for $C_{21}H_{26}O_4$: C, 73.66; H, 7.65. Found: C, 74.20; H, 7.63.

1',2',3',7',8',9',10',10a'-Octahydrocyclohepta[de]naphthalen-3'-ylidenesuccinic acid (**41a**)

The half-ester **41b** (1.02 g) was dissolved in methanol (50 mls) and a solution of potassium hydroxide (50 g) in water (50 mls) was added and the mixture stirred for one week. The methanol was evaporated and the residue was taken up in water and acidified. The diacid **41a** was extracted with benzene-ether, dried over magnesium sulphate, and concentrated to yield a light yellow crystalline solid (0.64 g). The acid was converted to the sodium salt which was recrystallized from water. The salt was converted back

into the acid which was recrystallized from benzene; m.p. 173.7-174.0°; i.r. (KBr) 2700-2500 and 940 (acid OH), 1705 (acid C=O), 1680 (conjugated acid C=O), 1655 cm^{-1} (C=C); mass spectrum (70 eV) *m/e* (relative intensity) 300.1369 (9, M_r ($^{12}C_{18}{}^{1}H_{20}{}^{16}O_4$) = 300.1362), 283 (17), 282 (84, $C_{18}H_{18}O_3$), 255 (19), 254 (100, $C_{17}H_{18}O_2$), 239 (5), 238 (12), 237 (10), 236 (9).

1',2',3',7',8',9',10',10a'-Octahydrocyclohepta[de]naphthalen-3'-ylidenesuccinic anhydride (**50**)

Vacuum sublimation of the diacid **41a** at 120-155°/ 0.005 mm gave as a white crystalline sublimate the octahydronaphthalenylidenesuccinic anhydride **50** : m.p. 165.2-165.4°; u.v. max. (95% C_2H_5OH) 204 (ε 1560), 215 (shoulder, ε 1100), 235 (ε 660), 307 nm (ε 1000 m^2 mol^{-1}); i.r. (Nujol) 1845, 1775, 1232 cm^{-1} (anhydride C=O); n.m.r. ($CDCl_3$) τ 2.43 (q, 1, 4'-*H*), 2.83 (m, 2, 5'-*H* and 6'-*H*), 6.33 (s, 2, C=C-C*H*$_2$CO$_2$), 7.2 (b, 3, C*H*C$_6$H$_3$C*H*$_2$), 7.6 (b, 2, C*H*$_2$C=C-CO$_2$), 8.3 p.p.m. (b, 8, alicyclic C*H*$_2$); mass spectrum (70 eV) *m/e* (relative intensity) 282.1249 (85, M_r ($^{12}C_{18}{}^{1}H_{18}{}^{16}O_3$) = 282.1257), 255 (19), 254 (100, $C_{17}H_{18}O_2$), 238 (9, $C_{17}H_{18}O$), 237 (10), 236 (8), 226 (5), 225 (7), 211 (16), 210 (26), 209 (39), 208 (20), 207 (9).

Anal. Calcd. for $C_{18}H_{18}O_3$: C, 76.57; H, 6.42. Found: C, 76.69; H, 6.42.

The hydrolysis-decarboxylation of the half-ester **41b** : *methyl 3-(1',2',3',7',8',9',10',10a'-octahydrocyclohepta-[de]naphthalen-3'-yl)propionate (**43b**); the lactone of 3-(3'-hydroxy-1',2',3',7',8',9',10',10a'-octahydrocyclohepta-[de]naphthalen-3'-yl)propionic acid (**42**).*

The half-ester **41b** (13.3 g) was refluxed with a solution of concentrated hydrochloric acid (100 mls), acetic acid (200 mls), and water (150 mls). Isolation of the product after 48 hours indicated that the hydrolysis-decarboxylation was incomplete* and the heating under reflux was continued with a fresh solution of the hydrochloric acid-acetic acid-water for an additional 72 hours. More hydrochloric acid (50 mls) was added after 24 hours and again after 48 hours of the second reflux period. The acidic solution was concentrated, benzene was added, and the mixture filtered to remove the highly insoluble cyclohepta-naphthalenylpropionic acid **44a** (3.4 g, 33%). The benzene

---

* A sample of the acid fraction of the incompletely reacted material was esterified with diazomethane and subjected to chromatography on alumina. The second fraction (5% of the total esters) obtained from the column contained, as the major component, an ester (i.r. 1735 cm^{-1}) which on v.p.c. on an SE30 column had retention time between that of the esters **43a** and **44a** and which had M_r = 270. This was presumably the methyl ester of the olefinic acid **51b** .

layer was separated, extracted with sodium carbonate solution, dried, and evaporated to give the lactone (1.8 g, 17%) as a gum. The sodium carbonate solution was acidified and extracted with benzene. From this benzene solution (3.8 g, 36%) of an acidic gum was isolated.

The combined acid fractions (7.9 g) which contained mainly the tetrahydro **44a** and octahydro **43a** cyclohepta-naphthalenylpropionic acids were taken up in a solution of ether (100 mls) and benzene (100 mls). Diazomethane (0.07 moles) in ether (200 mls) was added, with stirring to the solution at 0°. The mixture was stirred for 2 hours, stood at 5° for 12 hours, and the ether evaporated. The residue was taken up in benzene (5 mls) and placed on a column of alumina (300 g deactivated with 50% acetic acid (18 mls)). Elution with petroleum ether (900 mls) gave, after discarding the initial fraction (300 mls) methyl octahydrocycloheptanaphthalenylpropionate **43b** (2.2 g); i.r. (film) 1740 cm^{-1} (ester C=O); mass spectrum (70 eV) *m/e* (relative intensity) 272 (41, M_r ($C_{18}H_{24}O_2$) = 272), 241 (17, $C_{17}H_{21}O$), 240 (22), 199 (23), 198 (83), 186 (22), 185 (100), 158 (26). Further elution with petroleum ether (1800 mls) and then benzene (1200 mls) gave mixtures of the octahydro **43b** and tetrahydro esters **44b** (4.8 g). The ester mixtures were analysed by v.p.c. on an SE30 column and by mass spectrometry.

The neutral lactone fraction was recrystallized (x2) from ether-petroleum ether and sublimed (x2). The lactone **42** had m.p. 119.5-119.8°; i.r. (Nujol) 1775 cm^{-1} (lactone C=O), mass spectrum (70 eV) *m/e* (relative intensity) 256.1411 (59, M_r ($^{12}C_{17}{}^{1}H_{20}{}^{16}O_2$) = 256.1463), 238 (1, $C_{17}H_{18}O$), 212 (24, $C_{16}H_{20}$), 202 (16), 201 (100), 183 (21), 169 (18), 158 (41).

Anal. Calcd. for $C_{17}H_{20}O_2$: C, 79.65; H, 7.87. Found: C, 79.91; H, 7.89.

3-(1',2',3',7',8',9',10',10a'-Octahydrocyclohepta[de]naphthalen-3'-yl)propionic acid (**43a**)

The ester **43b** (1 g) in methanol (50 mls) was stirred with sodium hydroxide (50 g) in water (50 mls) for 5 days. The methanol was evaporated, the solution acidified and extracted with benzene. The benzene solution was dried and the solvent evaporated. The residual gum was recrystallized (x2) from methanol-water and sublimed at 120-125°/0.005 mm; m.p. 135-6.5°; i.r. (Nujol) 1705 cm^{-1} (acid C=O); n.m.r. (CCl_4) τ -1.6 (b, 1, CO_2H), 3.23 (s, 3, C_6H_3), 7.3 (b, $CH_2C_6H_3(CH)CHCH_2CH_2CO_2H$), 8.3 p.p.m. (b, alicyclic and aliphatic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 258.1615 (79, M_r ($^{12}C_{17}{}^{1}H_{22}{}^{16}O_2$) = 258.1620), 240 (5), 230 (8), 217 (9), 216 (9), 212 (20), 199 (16), 186 (29), 185 (100).

Anal. Calcd. for $C_{17}H_{22}O_2$: C, 79.03; H, 8.59. Found: C, 78.94; H, 8.59.

The reduction of lactone **42**.

The lactone **42** (5.6 g) was heated under reflux for 24 hours with a mixture of glacial acetic acid (125 mls), red phosphorous (7.5 g), iodine (2.5 g), and water (5 mls). The hot reaction mixture was filtered and added to water (400 mls) containing sufficient sodium bisulphite to reduce the iodine. The aqueous solution was extracted with benzene-ether and the benzene-ether solution then extracted with 10% sodium carbonate solution. The carbonate solution was acidified and extracted with benzene-ether. This benzene-ether solution was washed with water and concentrated to 200 mls. Diazomethane (0.04 moles) in ether (100 mls) was added and the mixture left to stand at 5° for 24 hours. The solvent was evaporated and the ester taken up in benzene and filtered through a column of alumina (100 g). Removal of the benzene gave the esters **43b** and **44b** (4.1 g, 79%).

The benzene-ether solution containing the non-acidic portion of the reaction product was dried and the solvent removed to yield 0.6 g of a gum shown by comparison of retention times with authentic samples (*vide infra*) to be composed of approximately equal parts of ketone **47** and 3-ethyl-7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene (**52**).

Methyl 3-(7',8',9',10'-tetrahydrocyclohepta[de]naphthalen-3'-yl)propionate (**44b**) and *3-ethyl-7,8,9,10-tetrahydrocyclohepta[de]naphthalene* (**52**)

A sample (12.7 g) of the mixed esters **43b** (80%) and **44b** (20%) was heated under an atmosphere of nitrogen with 30% palladium-on-carbon (0.8 g) in a Claisen flask fitted with a cold finger and placed in a silicone-oil bath. Hydrogen evolution started at 240°, reached a maximum at 270°, and continued for 8 hours as the temperature was raised to 300°. V.p.c. analysis after heating for 3.5 hours, at which time the temperature had reached 275°, showed only the tetrahydro **44b** (78%) and octahydro **43b** (22%) esters. The product was isolated by taking it up in benzene, filtering off the catalyst and evaporation of the solvent. V.p.c. analysis of the crude product showed the presence of the tetrahydro ester **44b** (95%) and its de-ethoxycarbonylation product, 3-ethyl-7,8,9,10-tetrahydrocyclohepta[*de*]naphthalene (**52**) (5%). Chromatography on alumina (300 g deactivated with 50% acetic acid (18 mls)) using petroleum ether then benzene as eluants gave a mixture (2.1 g) of **52** (25%) and **44b** (75%) and then pure ester **44b** (9.9 g).

The ester **44b** was distilled: b.p. 160-170°/0.2 mm; i.r. (film) 1735 cm^{-1} (ester C=O); n.m.r. (CCl_4) τ 2.29 (q, 1, 4'-*H*), 2.93 (m, 2, 5'-*H* and 6'-*H*), 3.03 (s, 2, 1'-*H*

and 2'-*H*), 6.50 (s, 3, CH_3O), 6.9 (b, 6, $C_{10}H_5CH_2$) 7.4 (m, 2, CH_2CO_2), 8.1 p.p.m. (b, 4, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 268.1468 (100, M_r ($^{12}C_{18}{}^{1}H_{20}{}^{16}O_2$) = 268.1463), 240 (15), 237 (14), 208 (17), 196 (31), 195 (99), 181 (19), 179 (21), 165 (40).

Anal. Calcd. for $C_{18}H_{20}O_2$: C, 80.56; H, 7.51. Found: C, 80.34; H, 7.70.

Further chromatography of the hydrocarbon-ester fraction on alumina, using petroleum ether as eluant, gave the hydrocarbon **52** (0.5 g) which was finally distilled: b.p. 120-122°/0.2 mm; n.m.r. (CCl_4) τ 2.23 (q, 1, 4-*H*), 2.87 (m, 2, 5-*H* and 6-*H*), 2.98 (s, 2, 1-*H* and 2-*H*), 6.8 (b, 4, $C_{10}H_5(CH_2)_2C_2H_4$) 7.0 (q, 2, *J* = 7 Hz, $CH_3CH_2C_{10}H_5$), 8.0 (b, 4, alicyclic CH_2), 8.69 p.p.m. (t, 3, *J* = 7 Hz, CH_3CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 210.1405 (100, M_r ($^{12}C_{16}{}^{1}H_{18}$) = 210.1408), 196 (33), 195 (98), 182 (27), 181 (92), 179 (29), 178 (25), 167 (40), 166 (38), 165 (97), 153 (30), 152 (46).

Anal. Calcd. for $C_{16}H_{18}$: C, 91.37; H, 8.63. Found: C, 91.29; H, 8.78.

3-(7',8',9',10'-Tetrahydrocyclohepta[de]naphthalen-3'-yl) propionic acid (**44a**)

The ester **44b** (1 g) in methanol (50 mls) was stirred with a solution of sodium hydroxide (50 g) in water (50 mls) for 5 days. The methanol was evaporated

and the solution acidified with hydrochloric acid. The acid **44a** was filtered off, recrystallized (x2) from acetic acid and sublimed: m.p. 193-193.5° (with sublimation), i.r. (Nujol) 1705 cm^{-1} (acid C=O); mass spectrum (70 eV) *m/e* (relative intensity) 254.1308 (100, M_r ($^{12}C_{17}{}^{1}H_{18}{}^{16}O_2$) = 254.1307), 196 (22), 195 (98), 165 (35).

Anal. Calcd. for $C_{17}H_{18}O_2$: C, 80.28; H, 7.13. Found: C, 80.80; H, 7.26.

1-Oxo-2,3,6,7,8,9-Hexahydro-1H-cyclohepta[gh]phenalene (**45**)

The ester **44b** (0.43 g) was stirred in anhydrous hydrogen fluoride (20 mls) at 20°. The polyvinyl chloride reaction vessel was enclosed and had a tube in the top. The other end of the tube was immersed in hydrogen fluoride in a second polyvinyl chloride container which was cooled in ice. This arrangement allowed the reaction to be carried out at room temperature without excessive loss of hydrogen fluoride. After 3 hours the hydrogen fluoride was evaporated in a stream of air. The product was taken up in benzene-ether and washed with water and with 5% sodium hydroxide solution. After drying over magnesium sulphate the solvent was evaporated. The residue was taken up in heptane and chromatographed on a column of acidic alumina (6 g, Brockmann activity II). Elution with petroleum ether and benzene-petroleum ether mixtures gave the ketone (0.35 g, 92%). Further elution with benzene removed a

bright yellow band of the enone **53** (4 mg). The ketone was recrystallized from pentane and then had m.p. 81-82°. A sample was sublimed at 79-80°/0.005 mm: m.p. 83.5-83.9°; u.v. max. (95% C_2H_5OH), 223 (ε 1600), 256 (ε 2000), 349 nm (ε 700 m^2 mol^{-1}); i.r. (Nujol) 1690 cm^{-1} (aromatic C=O); n.m.r. (CCl_4) τ 2.08 (nq, 1, *J* = 7.5 Hz, 11-*H*), 2.79 (nq, 1, *J* = 7.5 Hz, 10-*H*), 2.92 (s, 2, 4-*H* and 5-*H*), 6.8 (b, 6, $C_{10}H_4CH_2$), 7.27 (m, 2, $COCH_2$), 8.0 p.p.m. (b, 4, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 236.1206 (100, M_r ($^{12}C_{17}{}^{1}H_{16}{}^{16}O$) = 236.1201), 221 (3), 208 (4), 207 (6), 195 (6), 194 (6), 193 (11), 179 (14), 178 (9), 165 (13), 152 (6).

Anal. Calcd. for $C_{17}H_{16}O$: C, 86.40; H, 6.83. Found: C, 86.52; H, 6.92.

1-Oxo-6,7,8,9-tetrahydro-1H-cyclohepta[gh]phenalene (**53**)

2,3-Dichloro-5,6-dicyanoquinone (DDQ) (125 mg, 0.55 mmol), which had been recrystallized from benzene-chloroform, was dissolved in dry benzene (10 mls) and the solution was added with stirring to a solution of the ketone **45** (118 mg, 0.15 mmol) in benzene (10 mls). After stirring for 1 hour the solvent was evaporated and the residue extracted (x6) by heating with benzene (20 mls). The combined extracts were passed through a column of neutral alumina (6 g; Brockmann activity II). Elution with benzene (120 mls) gave a colourless fraction which was

the ketone **45** (13 mg, 11%) and a lime-green fraction which was the enone **53** (98 mg, 84%). A sample of the enone was recrystallized from methanol and sublimed at 125-128°/ 0.005 mm to give bright yellow crystals: m.p. 134.7-135.3°; u.v. max. (95% C_2H_5OH) 207 (ε 2300), 231 (ε 880), 259 (shoulder, ε 1800), 264 (ε 2100), 324 (ε 370), 326 (s, ε 630), 415 nm (ε 1050 m^2 mol^{-1}); i.r. (Nujol) 1635 cm^{-1} (aromatic and conjugated C=O); n.m.r. ($CDCl_3$) τ 1.58 (nq, 1, *J* = 7 Hz, 11-*H*), 2.42 (nq, 1, *J* = 10 Hz, 3-*H*), 2.52 (nq, 1, *J* = 7 Hz, 4-*H*) 2.55 (nq, 1, *J* = 7 Hz, 10-*H*), 2.74 (nq, 1, *J* = 7 Hz, 5-*H*), 3.41 (nq, 1, *J* = 10 Hz, 2-*H*), 6.76 (b, 4, $C_{10}H_4CH_2$), 8.0 p.p.m. (b, 4, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 234.1046 (100, M_r ($^{12}C_{17}{}^{1}H_{14}{}^{16}O$) = 234.1045), 219 (81), 218 (53), 206 (29), 205 (43), 202 (29), 193 (59), 191 (43), 189 (70), 178 (28), 177 (33), 176 (45), 165 (29), 152 (14).

Anal. Calcd. for $C_{17}H_{14}O$: C, 87.15; H, 6.02. Found: C, 87.17; H, 6.02.

2,3,6,7,8,9-Hexahydro-1H-cyclohepta[gh]phenalene (**46**)

The ketone **45** (0.50 g) in toluene (5 mls) was heated under reflux for 2 hours with amalgamated zinc (5 g), concentrated hydrochloric acid (10 mls), and acetic acid (20 mls). The mixture was cooled, diluted with water (120 mls), and extracted with ether (4 x 25 mls). The combined ethereal extract was washed with saturated bicarbonate

solution, dried over magnesium sulphate, and the solvent evaporated. The residue was chromatographed on alumina (Brockmann I) with heptane as eluant to give the hexahydrocycloheptaphenalene **46** (0.43 g, 92%). The hydrocarbon was recrystallized (x2) from methanol and sublimed at 100°/0.005 mm: m.p. 111.8-112.2°; u.v. max. (95%, C_2H_5OH) 236 (ε 2200), 275 (shoulder, ε 370), 288 (s, ε 700), 298 (ε 880), 309 (s, ε 660), 316 (ε 480), 325 (ε 190), 331 nm (ε 300 m^2mol^{-1}); i.r. (Nujol) 3070, 3035, 1610, 1595, 830 cm^{-1} (aromatic with two adjacent H); n.m.r. (CCl_4) τ 3.09 (s, 4, $C_{10}H_4$), 7.0 (b, 8, $C_{10}H_4CH_2$), 8.1 p.p.m. (b, 6, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 222.1405 (100, M_r ($^{12}C_{17}{}^{1}H_{18}$) = 222.1408), 208 (6), 207 (32), 194 (29), 193 (15), 181 (12), 179 (25), 178 (19), 165 (25).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.91; H, 8.18.

1-Oxo-1,2,3,3a,5,5a,6,7,8,9-decahydro-4H-cyclohepta[cd] phenalene (**47**)

The ester **43b** (0.73 g) was heated on a steam bath with a solution of phosphorus pentoxide (25 g) in 85% orthophosphoric acid (24 g) for 2 hours. The mixture was poured into ice-water (100 g) and extracted with benzene-ether (4 x 50 ml). The extract was washed with 5% sodium hydroxide solution (3 x 50 ml), dried, and the solvent

evaporated, yielding the ketone **47** (0.60 g, 93%). A sample was recrystallized from hexane, sublimed at 80-85°/0.01 mm and recrystallized (x3) from methanol; m.p. 85.0-86.5°; u.v. max. (95% C_2H_5OH) 219 (ε 1400), 269 nm (ε 1000 m^2 mol^{-1}); i.r. (melt) 1680 cm^{-1} (aromatic ketone C=O); n.m.r. (CCl_4) τ 2.35 (nq, 1, *J* = 7.5 Hz, 11-*H*), 3.07 (nq, 1, *J* = 7.5 Hz, 10-*H*), 7.3 (b, 6, C_6H_2CH, $C_6H_2CH_2$, $COCH_2$), 8.2 p.p.m. (b, 12, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 240.1521 (100, M_r ($^{12}C_{17}{}^{1}H_{20}{}^{16}O$) = 240.1514), 223 (8), 210 (21), 197 (16), 196 (45), 195 (13), 194 (19), 183 (21), 182 (57), 181 (56), 167 (22), 165 (12), 163 (14), 154 (22), 153 (33), 152 (13), 151 (21), 140 (21), 139 (60).

Anal. Calcd. for $C_{17}H_{20}O$: C, 84.95; H, 8.39. Found: C, 84.90; H, 8.57.

1, 2, 3, 3a, 5, 5a, 6, 7, 8, 9-Decahydro-4H-cyclohepta[cd]phenalene (**48**)

The ketone **47** (1 g) was reduced following the procedure described for the reduction of the ketone **14**. The hydrocarbon **48** (0.81 g, 88%) was obtained on chromatography of the crude product and then was distilled; m.p. 60.2-61.5°; b.p. 90°/0.007 mm; i.r. (melt) 3070, 3035, and 3015 (aromatic C-H), 2930 and 2860 (aliphatic C-H), 1595 and 1475 (aromatic ring), 1450 (CH_2 bending), 840, 830 (aromatic C-H bending) 805, 790 cm^{-1}; u.v. max. (95% C_2H_5OH) 211 (ε 1430), 224 nm (shoulder, ε 870 m^2 mol^{-1}); n.m.r.

(CCl_4) τ 3.32 (s, 2, C_6H_2), 7.3 (b, 6, C_6H_2CH, $C_6H_2CH_2$), 8.3 p.p.m. (b, 14, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 226.1716 (100, M_r ($^{12}C_{17}{}^{1}H_{22}$) = 226.1721), 199 (6), 198 (36), 197 (16), 185 (17), 184 (20), 183 (34), 170 (19), 169 (42), 155 (12).

Anal. Calcd. for $C_{17}H_{22}$: C, 90.20; H, 9.80. Found: C, 90.16; H, 9.88.

5,5a,6,7,8,9-Hexahydro-4H-cyclohepta[cd]phenalene (**49**)

The decahydrocycloheptaphenalene **48** (0.2 g) was heated under an atmosphere of nitrogen with 30% palladium-on-carbon (0.02 g) at 300° for 4 hours. The product was taken up in benzene, the catalyst filtered off and the benzene evaporated. V.p.c. and mass spectral analysis of the residue showed that it was a mixture of unchanged decahydro compound **48** (4%) and the isomeric hexahydrocycloheptaphenalenes **46** (23%) and **49** (73%). When the decahydrophenalenone **47** (0.2 g) was heated with palladium-on-carbon under the conditions described the product consisted of unreacted ketone **47** (7%) and the hexahydrocycloheptaphenalenes **46** (24%) and **49** (69%).

The combined products from the two dehydrogenations (0.31 g) were taken up in benzene (0.5 mls) and chromatographed on alumina (10 g of activity I). The more symmetrical hexahydrocyclohepta[*gh*]phenalene was eluted first with petroleum ether. Further elution with petroleum ether and

with 5% benzene-petroleum ether gave the hexahydrocyclohepta [*cd*]phenalene contaminated with the *gh* isomer. The impure *cd* isomer was rechromatographed. The final fractions from the second column were recrystallized (x2) from methanol and then sublimed at 65-70°/0.005 mm to give the pure hexahydrocyclohepta[*cd*]phenalene **49** as a white powder: m.p. 73.3-74.3°; u.v. max. (95% C_2H_5OH) 236 (ε 2000), 271 (shoulder, ε 360), 281 (s, ε 600), 292 (ε 720), 297 (s, ε 640), 303 (s, ε 550), 311 (s, ε 310), 315 (s, ε 200), 325 (ε 140), 330 nm (s, ε 80 m^2 mol^{-1}); n.m.r. (CCl_4) τ 2.83 (m, 5, $C_{10}H_5$), 7.03 (b, 5, $C_{10}H_5CH$, $C_{10}H_5CH_2$), 8.15 p.p.m. (b, 8, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 222.1397 (100, M_r ($^{12}C_{17}{}^{1}H_{18}$) = 222.1408), 207 (4), 193 (17), 181 (13), 179 (12), 178 (11), 165 (41).

Anal. Calcd. for $C_{17}H_{18}$: C, 91.84; H, 8.16. Found: C, 91.65; H, 8.33.

The hydrogenation of the enone **53** to the ketone **45**.

The enone **53** (20 mgm) was dissolved in anhydrous benzene and stirred overnight with platinum oxide (5 mgm) under a pressure of hydrogen slightly greater than atmospheric. The catalyst was filtered off and the solvent evaporated to yield 20 mgm of a white solid which had identical properties (i.r., v.p.c.) to those of an authentic sample of ketone **45**.

Catalytic hydrogenation of the ketone **45**.

The ketone **45** (116 mgm) containing a small amount of enone **53** was dissolved in anhydrous benzene and stirred for four days with 10% palladium-on-carbon (120 mgm) under hydrogen. Nearly a four molar volume of hydrogen was absorbed before uptake ceased. The catalyst was filtered off, the solvent evaporated, and the residue dried under vacuum. V.p.c. analysis of the residue (116 mgm) indicated that of the volatile components the hydrocarbon **46** was the main product. However, mass spectrum (70 eV) *m/e* (relative intensity) 219 (70), 220 (100), 221 (9), 222 (14), 224 (7), 236 (4) and ions of higher masses suggest that the desired hydrocarbon (M^{+} = 222) was only a minor product.

The treatment of the hydrocarbon **46** with mineral acid.

The hydrocarbon **46** (22 mgm) was stirred for four days with 1% ethanolic hydrochloric acid (5 mls). The products were extracted by diluting the reaction mixture with two volumes of water and extracting with benzene. The combined benzene layers were washed with bicarbonate solution, dried over magnesium sulphate, and concentrated. A comparative v.p.c. analysis of the concentrate indicated the major volatile product to be the enone **53**. Little starting material was evident. Infrared showed the carbonyl stretching frequencies of the ketone **45** (1690 cm^{-1}) and the enone **53** (1635 cm^{-1}) to be of weak and medium

intensities, respectively. Significant mass spectrum peaks were: (70 eV) *m/e* (relative intensity) 219 (56), 220 (33), 221 (25), 222 (52), 223 (15), 226 (33), 234 (80), 235 (30), 236 (100), 237 (25), and peaks of lower intensities at higher masses.

The Synthesis of *5,6,7,8-Tetrahydrocyclohepta[fg]acenaphthene* (**57**)

4-(5'-Acenaphthyl)-4-oxo-butanoic acid (**55a**).

Succinic anhydride (110 g, 1.1 moles) and finely crushed aluminium chloride (320 g, 2.2 moles) were stirred mechanically in a 3-litre three-necked flask containing dichloroethane (1 litre) which had been dried by distillation over phosphorus pentoxide. When this light yellow coloured mixture had been cooled to 0° in an ice-salt bath, acenaphthene (**54**, 154 g, 1.0 mole) was added during 30 minutes. The mixture was stirred for a further hour at 0° before being allowed to come to room temperature. After a total of 4 hours stirring it was stood overnight.

The bright orange gelatinous product was poured into 20% hydrochloric acid-ice water (1.2 litres) and the dichloroethane removed by reduced pressure distillation. The aqueous layer was then filtered off and the product acid washed with water before being dissolved in 2 litres of hot water containing 450 g of sodium carbonate decahydrate.

This solution was filtered hot and after the addition of 400 g of sodium chloride it was allowed to cool. The resulting precipitate was filtered off, washed free of the dark mother liquor with saturated brine, and then recrystallized from 1.5 litres of hot water to which was added 150 g of sodium chloride before it was allowed to cool. The sodium salt of the butanoic acid gave clean fibrous crystals which were collected and washed with saturated brine, and then acidified with 1 litre of 20% hydrochloric acid. The bulky white precipitate was filtered off and washed several times with water until the washings were no longer acidic. The acid was dried by warming it in a hot air oven at 45°: m.p. = 206° with decomposition (cf 208°[39]); i.r. (Nujol) 2700-2500 (CO.O-H), 1700 (acid C=O), 1670 (aromatic C=O) 1600 cm^{-1} (naphthalene ring).

Methyl-4-(5'-acenaphthyl)-4-oxo-butanoate (**55b**)

The keto acid **55a** (202 g) was refluxed for 8 hours with mathanol (1 litre) and concentrated sulphuric acid (50 mls). When the solution cooled 187 g of fibrous crystals formed and these were filtered off. The filtrate was neutralised with 5% aqueous sodium hydroxide to yield 8.7 g of unreacted acid as a solid and 18 g of crude ester which was extracted from the concentrate of the filtrate from the latter precipitate. The first crop of ester crystals was recrystallized twice from methanol to yield 182 g

(85%) of light beige plates (previous samples were light yellow): m.p. = 80-82° (cf 89°[39]); i.r. (Nujol) 1740 (ester C=O), 1670 (aromatic C=O), 1600 cm^{-1} (naphthalene ring); n.m.r. ($CDCl_3$) τ 1.23 and 1.40 (nq, 1, $J^{APP}_{6'7'}$ = 8 Hz, $H_{6'}$), 1.90 and 2.02 (nq, 1, $J^{APP}_{3'4'}$ = 7.5 Hz, $H_{4'}$), 2.32, 2.45, 2.47, and 2.58 (q, 1, $J^{APP}_{6'7'}$ = 8 Hz, $J^{APP}_{7'8'}$ = 7 Hz, $H_{7'}$), 2.67 and 2.78 (nq, 1, $J^{APP}_{7'8'}$ = 7 Hz, $H_{8'}$), 2.73 and 2.86 p.p.m. (nq, 1, $J^{APP}_{3'4'}$ = 7.5 Hz, $H_{3'}$); u.v. max. (95% C_2H_5OH) 231 (ε 1450), 244 (ε 1630), 332 nm (ε 780 m^2 mol^{-1}); mass spectrum (70 eV) *m/e* (relative intensity) 268.109 (90, M_r ($^{12}C_{17}{}^{1}H_{16}{}^{16}O_3$) = 268.110), 238 (32), 183 (53), 182 (100), 155 (13), 154 (82), 153 (70), 152 (25), 91 (23), 90 (13), 85 (20).

5,8-Dioxo-5,6,7,8-tetrahydrocyclohepta[fg]acenaphthene (**56**)

A melt was prepared by heating at 150° in a 250 ml round-bottomed flask anhydrous aluminium chloride (125 g) and dried sodium chloride (25 g). To this was added the ester **55b** (20 g). The yellow melt changed to a bright red colour and the temperature rose to 170°, but quickly dropped to 140° when the heat source was removed. Heating was resumed for 10 minutes by which time the temperature had increased to 170°. The dark flux was dissipated by pouring into 500 mls of ice water. After cooling the dark solid was filtered and dried under vacuum. The precipitate was then refluxed overnight with 150 mls of benzene. The

benzene was decanted off, cooled, dried over magnesium sulphate, and then columned on 200 g of 5% aqueous deactivated basic alumina (32 x 3 cm). The first fraction, eluted with 500 mls of benzene, was a dense salmon-pink colour and weighed 0.15 g. The infrared spectrum of this solid was identical to that of an authentic sample of the starting material ester. The second fraction, eluted with 1,500 mls of benzene, was orange and concentrated to 9.73 g (55%) of a solid which was mainly the diketone **56** but which also contained traces of the ester. The third fraction comprised a dark band trailing the orange band and was eluted with chloroform. It concentrated to 0.25 g of tarry material and was discarded. Before being hydrogenated the diketone was purified further by sublimation at 175°/0.005 mm. However, this was probably unnecessary, as the column eluants were pure enough for hydrogenation. For an analytical sample the diketone was recrystallized from ethanol to give fine yellow needles: m.p. = 175-6° (cf 180°[39]); i.r. (Nujol) 1660 (aromatic C=O), 1600 cm^{-1} (naphthalene ring); n.m.r. ($CDCl_3$) τ 1.44, 1.56, 2.52, and 2.64 (q, 4, $J_{34} = J_{910}$ = 7.5 Hz, H_4, H_9 and H_3, H_{10}), 6.57 (s, 4, H_1's and H_2's), 6.95 p.p.m. (s, 4, H_6's and H_7's); u.v. max. (95% C_2H_5OH), 217 (ε 1350), 245 (ε 2000), 351 nm (ε 1,000 m^2 mol^{-1}); mass spectrum (70 eV) *m/e* (relative intensity) 236.083 (100, M_r ($^{12}C_{16}{}^{1}H_{12}$) = 236.084) 235 (91), 209 (9), 208 (7), 207

(15), 181 (39), 180 (94), 153 (22), 152 (86), 151 (61), 150 (30).

Unsuccessful Attempts:

1. With anhydrous hydrogen fluoride: The ester **55b** (0.96 g) was stirred for 12 hours with anhydrous hydrogen fluoride (50 mls). The PVC flask was then stood overnight and the hydrogen fluoride was allowed to evaporate. The evaporation of the hydrogen fluoride was completed by blowing air into the vessel and resuming stirring. The products were extracted by treating the reaction mixture with 25 mls of water and 50 mls of ether-benzene. The water-solvent mixture was filtered through a hydrogen fluoride-resistant sintered funnel to remove an insoluble precipitate. The solid had infrared characteristics of the free acid **55a**. The organic layer in the filtrate was separated, washed with water (3 x 500 mls), and then dried over magnesium sulphate with simultaneous treatment with norite. After filtration the solvent was evaporated to yield 0.47 g of a tawny solid whose infrared spectrum was identical to the starting material.

2. With aluminium chloride in refluxing dichloroethane: The ester **55b** (1.34 g, 0.005 moles) and finely crushed aluminium chloride (1.34 g, 0.01 moles) were refluxed in 10 mls of dichloroethane. Some brilliant colours were observed during the reaction, the initial yellow colour

at first giving a dark coloration which cleared to cherry red followed by amber and finally a dense green. 1 ml samples were withdrawn after 0.25, 1, and 5 hours, and the reaction stopped after 18 hours. The products were extracted by treating the reaction mixture with 10% hydrochloric acid and washing the aqueous layer with chloroform. G.l.c. analysis of all samples showed only one peak corresponding to that of a sample of the ester starting material. Infrared analysis of the final product indicated the presence of a small amount of free acid **55a**.

5,6,7,8-Tetrahydrocyclohepta[fg]acenaphthene (**57**).

The diketone **56** (2.36 g, 0.01 moles) was dissolved in chloroform (100 mls) and stirred magnetically with 5% palladium-on-carbon (0.2 g) under hydrogen at a pressure slightly greater than atmospheric. The uptake of hydrogen was measured accurately using a gas burette, and when 0.04 moles (956 mls at 21° C and 770 mm) of hydrogen had been absorbed the product was isolated by filtering off the catalyst and evaporating the solvent. The tan residue weighed 2.1 g and v.p.c. analysis using a 5' SE-30 column at 270° indicated that the product was mainly the desired tetrahydroacenaphthene **57** (1.1 minutes from injection) along with traces of the octahydroacenaphthene **59** (0.8 mins), the monoketone **58** (1.7 mins), and the ester **55b** (2.4 mins), of which there were traces in the starting

material. The product was purified by dissolving it in 10 mls of benzene and columning it through 50 g (15 x 300 mm) of activity I basic alumina. The first fraction was eluted with 150 mls of pentane followed by 100 mls of benzene. Evaporation of the solvent gave 1.99 g (96%) of white needles which v.p.c. indicated to be more than 99% of the desired hydrocarbon **57** . The impurity was the octahydro-acenaphthene **59**. The second fraction which was a pink band was eluted with ether and weighed 0.046 g. V.p.c. analysis showed it to contain the monoketone **58** along with the ester **55b** and the hydrocarbon **57**. The third fraction, eluted with chloroform, contained 0.03 g of the monoketone **58**. The first fraction was further purified by recrystallization from ethanol: m.p. 136.5-137.3° (cf 138°[39]); i.r. (melt) 3075, 3040, 3022 (aromatic C-H), 2935, 2865 (aliphatic C-H), 1605, 1594, (naphthalene ring), 837, 823, 792 cm^{-1} (C-H bending); n.m.r. (CCl_4) τ 3.07 (s, 4, $C_{10}H_4$), 6.77 (s, 4, H_1's and H_2's), 6.9 (m, 4, H_5's and H_8's), 8.0 p.p.m. (m, 4, H_6's and H_7's); u.v. max. (95% C_2H_5OH) 236 (ε 1880), 252 (ε 140), 277 (ε 370), 289 (ε 670), 298.5 (ε 850), 302 (ε 800), 310.5 (ε 625), 316.5 (ε 560), 324.5 (ε 210), 331 nm (ε 460 m^2 mol^{-1}); mass spectrum (70 eV) *m/e* (relative intensity) 208.1251 (100, M_r ($^{12}C_{16}{}^{1}H_{16}$) = 208.1252), 207 (66), 193 (53), 191 (35), 189 (24), 180 (62), 179 (46), 178 (33), 167 (22), 166 (16), 165 (61), 153 (16), 152 (28), 151 (11), 95 (15), 89 (17).

Other methods used to reduce the diketone :

1. Wolff-Kishner reduction.[39] The diketone **56** (2.36 g, 0.01 mole) and hydrazine hydrate (1.0 ml, 0.02 mole) were refluxed for 8 hours with a solution of sodium (1.8 g, 0.8 mole) in 25 mls of dry ethanol. The reaction mixture was treated with water and extracted with benzene-ether (4 x 25 mls). The organic layer was dried over magnesium sulphate, concentrated, and the residue taken up in 20 mls of benzene and columned through 50 g (15 x 300 mm) of activity I basic alumina in pentane. 200 mls of pentane and 100 mls of benzene eluted 1.05 g (50%) of the hydrocarbon **57**. When the column was eluted with chloroform a small amount of an unidentified bright red compound was collected.

2. A modified Wolff-Kishner reduction[106]: The diketone **56** (1.18 g, 5 mmoles) was refluxed for 0.5 hour with ethanol (20 mls) and hydrazine hydrate (5 mls, 0.1 mole). When the reaction mixture was concentrated to 10 mls and 10 mls of water was added to it, fine, light yellow needles precipitated out. These were filtered off and after vacuum drying weighed 1.0 g (76%) and melted at 182-5°. The mother liquor was concentrated to 5 mls and yielded a further 0.31 g of darker crystals which when recrystallized from ethanol-water gave 0.21 g (15%) of crystals melting at 180-3°, bringing the total yield of

dihydrazone to 91%.

The dihydrazone (1.32 g, 5 mmoles) was reduced by refluxing it for 2.5 hours with potassium tertiary butoxide (1.92 g, 15 mmoles) in 20 mls of sodium dried toluene. Most of the nitrogen evolution had ceased by the end of the first hour of refluxing. The solution was at first a dense green colour but later turned crimson with some tarring. The product was isolated by adding the cooled reaction mixture to 50 mls of water and extracting with ether (4 x 20 mls). The combined extracts were dried over magnesium sulphate and concentrated to yield 1.03 g of a dark solid. This was taken up in 10 mls of benzene and columned on 10 g (12 x 110 mm) of activity I neutral alumina. Elution with 80 mls of petroleum ether yielded 0.84 g (81%) of v.p.c. pure hydrocarbon. Elution with ether gave 0.05 g of dark residue which included a compound which was crimson on the column. The yield of 81% for this reaction combined with a yield of 91% for the preparation of the dihydrazone gives an optimum yield for the production of hydrocarbon **57** from **56** of 74%.

3. Low temperature Wolff-Kishner reduction[78]:
The dihydrazone (prepared as above, 0.66 g, 2.5 mmoles) in 5 mls of anhydrous dimethyl sulphoxide was treated dropwise over 4 hours with anhydrous potassium tertiary butoxide (1 g, 10 mmoles) in 5 mls of dimethyl sulphoxide.

The mixture was refluxed overnight and the products then extracted with water and dichloromethane. The aqueous layer was separated and washed further with dichloromethane. The organic layers were combined, washed with water, dried over magnesium sulphate, and concentrated to yield 289 mgm of tar. This was taken up in benzene and columned on 10 g of activity I basic alumina. Benzene eluted only 5 mgm of the desired hydrocarbon. Elution with chloroform gave 8 mgm of an unidentified bright red compound.

4. Clemmensen reduction: The diketone **56** (0.3 g) was dissolved in 5 mls of toluene and then added to a mixture of concentrated hydrochloric acid (10 mls), acetic acid (20 mls) and amalgamated zinc (5 g). The amalgam had been prepared beforehand by swirling 5 g of powdered zinc and 0.5 g of mercuric chloride with dilute hydrochloric acid. The reaction was brought to reflux within 5 minutes and the organic layer turned a dark crimson colour which later turned to amber and finally became clear. 0.5 ml samples were withdrawn from the toluene layer after 0.5, 1, 5.5, and 16 hours of refluxing, and the reaction finally was stopped after 216 hours. The products were extracted from each sample by treating the toluene layer with water, separating the aqueous layer, and extracting it with ether (2 x 5 mls). The organic layers were combined, extracted with sodium bicarbonate solution, dried over magnesium

sulphate, and concentrated. The dark residues were dissolved in chloroform and analysed by v.p.c. using a 5' SE-30 column at 270°. V.p.c. showed that even after only 0.5 hours refluxing not only had all the diketone been reduced but that 40% of the tetrahydro compound **57** had been reduced to the octahydro compound **59**. It was surprising then that after 216 hours of refluxing only 56% of the hydrocarbons was the octahydro compound. Considerable amounts of tar were also produced.

5-Oxo-5,6,7,8-tetrahydrocyclohepta[fg]acenaphthene (**58**)

This compound (0.4 g) was isolated when the hydrogenation of 2.36 g (0.01 mole) of the diketone was terminated before the required amount of hydrogen (presumably about 100 mls or 10% of the required amount) was absorbed. The monoketone was isolated in a fairly pure state in the third fraction of a column similar to the one cited on page 139. It was further purified by recrystallizations from ethanol: m.p. = 123.0-124.0°; i.r. (Nujol) 1655 (aromatic C=O), 1610 and 1600 cm^{-1} (aromatic ring); n.m.r. (CCl_4) τ 2.26 and 2.82 (q, 2, J = 7 Hz, H_4 and H_3), 2.86 (s, 2, H_9 and H_{10}), 6.7 (s, 4, H_1's and H_2's), 6.93 (t, 2, J = 5 Hz, H_8's), 7.17 (t, 2, J = 6.5 Hz, H_6's), 7.72 p.p.m. (m, 2, H_7's); u.v. max. (95% C_2H_5OH) 216 (ε 1030), 227 (ε 890), 250 nm (ε 910 m^2 mol^{-1}); mass spectrum (70 eV) *m/e* (relative intensity) 222.1040 (100, M_r

($^{12}C_{16}{}^{1}H_{14}{}^{16}O$) = 222.1045), 221 (35), 207 (31), 205 (15), 195 (30), 194 (91), 193 (84), 191 (33), 189 (39), 181 (15), 180 (19), 179 (34), 178 (37), 167 (32), 166 (92), 165 (99), 164 (38), 163 (39), 153 (21), 152 (46), 151 (20), 139 (24), 97 (40), 94.5 (22), 89 (23), 83 (26), 82.5 (50), 82 (55).

Anal. Calcd. for $C_{16}H_{14}O$: C, 86.45; H, 6.35. Found: C, 86.32; H, 6.36.

2a,3,4,4a,5,6,7,8-Octahydrocyclohepta[fg]acenaphthene (**59**)

This compound was detected in the products of the catalytic hydrogenation of the diketone **56** when the hydrogen uptake was allowed to exceed the required four molar amount, or when the reduction was carried out overnight in a high pressure hydrogenator. 250 mgms were isolated free of the tetrahydro compound **57** when 0.7 g of over-reduced product containing about 50% of the octahydro compound were dissolved in 1 ml of benzene and columned on 50 g (300 x 15 mm) of activity I basic alumina. 200 mls of pentane eluant brought down pure octahydro compound before the fifth column length eluted a mixture of the two hydrocarbons. The concentrate of the first fractions was recrystallized from ethanol to yield 43 mgms of white crystals melting at 50.0-50.4°. The mother liquor was concentrated to 1 ml and yielded, after three washings with ethanol, 55 mgms melting at 49.8-50.5°: i.r. (melt) 3025 (aromatic C-H), 2930 and 2860 (aliphatic C-H), 1605 and 1475 (aromatic ring),

1450 (CH_2 bending), 843, 832 (aromatic C-H bending), 807, 789; n.m.r. (CCl_4) τ 3.27 (s, 2, C_6H_2), 6.9-7.5 (m, 6, $CHC_6H_2CH_2$), 7.5-9.1 p.p.m. (m, 12, alicyclic CH_2); u.v. max. 209 (ε 1390), 221 (ε 930), 226 nm (ε 850 m^2 mol^{-1}); mass spectrum (70 eV) *m/e* (relative intensity) 212.1562 (100, M_r ($^{12}C_{16}{}^{1}H_{20}$) = 212.1565), 211 (12), 184 (55), 183 (27), 171 (18), 170 (35), 169 (41), 156 (24), 155 (39), 141 (20), 129 (13), 128 (16), 115 (14).

Anal. Calcd. for $C_{16}H_{20}$: C, 90.51%; H, 9.49%. Found: C, 90.43%, H, 9.43%.

Attempts to Form Eight-membered Carbocyclic *Peri*-naphthalenes by the Ring Expansion of the Ketones **30** and **56**

Reagents: *Diazomethane* was prepared by a method which was an adaption of that of Moore and Reed[107]. Diazomethane is explosive and toxic. It should not be exposed to sunlight nor to sharp edges. If a solution of it is to be stirred a teflon covered stirring bar should be used. 500 mls of USP ether, 90 mls of diethylene glycol monoethyl ether, and 120 mls of 30% aqueous sodium hydroxide were placed in a 1 litre one-piece distilling apparatus. (It was of continuous glass from still pot to receiver tip. There were no ground glass joints and the aperture above the still pot was sealed with a rubber bung.) The solutions were cooled to at least 0° in an ice-salt bath and 36 g (0.1 mole) of bis (N-methyl-N-nitroso)terephthalamide (70%

in mineral oil) were added. The apparatus was immediately transferred to a heating mantle. Shortly after the addition of the terephthalamide a yellow gas was given off and this and the ether-diazomethane solution which was later distilled over was collected in an ice-cooled receiver. The receiving flask contained smooth pellets of potassium hydroxide and a small layer of anhydrous ether so that the receiving tip of the distilling apparatus was submerged. About 400 mls of ether was distilled over to give a solution of diazomethane which was usually about 0.4 M. The molarity of the diazomethane solution was calculated after titrating with 17.5 N AR acetic acid. When all the diazomethane had been neutralised the solution was no longer yellow.

Boron trifluoride etherate was purified after the manner of Zweifel and Brown[108]. Approximately 7 mls of technical boron trifluoride etherate, 1 ml of anhydrous ether, 0.2 g of sodium hydride dispersion, and a boiling chip were placed in a 25 ml distilling apparatus. The apparatus had just previously been flamed out under vacuum and flushed with nitrogen. The distillation was conducted under aspirator vacuum and the fraction collected boiled constantly at 52°. It was stored under nitrogen.

The Attempted Ring Expansion of the Ketone **30**

The ketone **30** (254 mgm, 1 mmole) was dissolved in chloroform (50 mls) and methanol (25 mls) and cooled to 0°. To this was added 25 mls of 0.4 M diazomethane solution (10 mmoles) and the solution was stirred for 10 minutes. A sample was withdrawn after the reaction had stood at 0° for 12 hours. I.r. and v.p.c. analysis of the concentrate were identical to that for the starting material, ketone **30**. When the reaction solution was stirred for 2 hours at room temperature, by which time the yellow coloration of the diazomethane had almost disappeared, the v.p.c. retention time and i.r. spectrum of the product were still unchanged. The product was purified by columning it on 10 g of 5% aqueous deactivated acidic alumina (13 x 95 mm). The product (244 mgm) was eluted with 42-48 petroleum ether and 10% benzene-petroleum ether. After recrystallization from pentane the solid melted at 70.5-71.5° (cf 73.5-74.5° for an authentic sample of **30**) and its n.m.r. spectrum was the same as that of the ketone **30**.

Another reaction was run in which the ketone **30** (254 mgm, 1 mmole) was dissolved in 10 mls of anhydrous benzene and treated with 14.2 µl (0.1 mmole) of distilled boron trifluoride etherate. 20 mls of 0.4 M ethereal diazomethane were then added over 20 minutes. At first the yellow colour of the diazomethane solution was dissipated immediately with vigorous gas evolution, but by the

time the addition was complete the yellow colour persisted. A sample withdrawn after 1 hour of reaction had no change in its v.p.c. retention time so the reaction mixture was treated with a further 130 µl (0.9 mmole) of boron trifluoride etherate followed by 50 mls of diazomethane solution. The solution was stirred for a further two hours before being washed with 10% aqueous potassium fluoride, dried over magnesium sulphate, and concentrated. I.r. and v.p.c. analyses indicated no change in the starting material.

The Attempted Ring Expansion of the Diketone **56**

The method used for this reaction generally followed that of Johnson *et al*[109]. The diketone **56** (0.472 g, 2 mmoles) was dissolved in 20 mls of anhydrous dichloromethane and treated with 0.028 g (0.2 mmole, or 5 equivs %, considering the two carbonyl functions) of freshly distilled boron trifluoride etherate. The solution was stirred at 0° under an atmosphere of nitrogen and to it was added 50 mls of 0.3 M diazomethane solution over 30 minutes. A further 30 mls of dichloromethane was added after 15 minutes because the ether of the diazomethane solution caused the diketone to crystallize out of solution. Stirring was continued for a further 90 minutes at 0° before the solution was stood overnight at room temperature. The colourless solution was then washed with aqueous 10% potassium fluoride

solution and dried over magnesium sulphate. V.p.c. and i.r. analyses of the concentrated product indicated that only the starting material was present.

The Attempted Fluorination of α-Substituted Carbocyclic Naphthalenes

The attempted fluorination of 1-bromo-1-phenylthane using anhydrous hydrogen fluoride and mercuric fluoride

1-Bromo-1-phenylethane: Ethyl benzene (32 g, 0.3 mole) was warmed with N-bromosuccinimide (N.B.S.) (47.8 g, 0.27 mole) in distilled carbon tetrachloride (150 mls). Benzoylperoxide (0.2 g) was used as a catalyst. When the reaction had been initiated (after 5-10 minutes) the heating mantle was removed. The reaction was complete when the N.B.S. at the bottom of the flask had all dissolved and been converted to succinimide which floated on the surface of the carbon tetrachloride. After cooling, the succinimide was filtered off and the carbon tetrachloride evaporated. The residue was distilled to give 40.5 g (82% based on N.B.S.) of product: b.p. 94-5°/18 mm (cf 86-8°/15 mm[1]).

Bromide-fluoride exchange was attempted by three methods: anhydrous hydrogen fluoride at -78° for 2 hours; anhydrous hydrogen fluoride at room temperature for 10 minutes; anhydrous hydrogen fluoride and mercuric oxide at

-78° for 2 hours. 1-Bromo-1-phenylethane (4.6 g, 0.025 mole) dissolved in dichloromethane was used in each reaction. 10-20 mls of anhydrous hydrogen fluoride were used and in the last case it was treated with 5.4 g (0.025 mole) of mercuric oxide. The reaction mixtures were stirred magnetically in screw-top PVC containers and after their respective reaction times had elapsed were poured onto ice. The melted ice solution was extracted with ether-benzene which in turn was extracted with water and bicarbonate solution. The organic layer was then dried and concentrated. In the reactions in which anhydrous hydrogen fluoride was the sole reagent only the starting material was reclaimed (v.p.c., i.r.). The product from the mercuric fluoride catalysed reaction, a bright yellow crystalline solid, was not identified but was clearly not the desired product: i.r.: no ν_{C-F}; n.m.r. (CCl_4) τ 2.9, 3.0 (2xs, 5, aromatic H), 6.0 (m, 1, methine H), 8.4 p.p.m. (d, 4, CHX-CH_3); mass spectrum (70 eV) *m/e* (relative intensity) 204 (7), 202 (23), 200 (20), 149 (9), 120 (16), 105 (93), 77 (100).

The attempted fluorination of 1-bromo-1-phenylethane using silver fluoride

Silver fluoride: Silver (I) fluoride (c.a. 1.5 g) was prepared by dissolving 6 g of silver carbonate in a minimal amount of 52% aqueous hydrogen fluoride. 50 mls of methanol were then added and the mixture was filtered through

a polyethylene sintered funnel. The silver fluoride was precipitated from the filtrate by adding it to 200 mls of ether. The yellow salt was filtered off and dried under vacuum. Silver fluoride must be stored in the dark as it is photosensitive.

1-Bromo-1-phenylethane (0.46 g, 2.5 mmoles) was stirred overnight at room temperature with silver (I) fluoride (0.63 g, 5 mmoles) in acetonitrile (5 mls) which had been dried and distilled over phosphorus pentoxide. During the reaction light was excluded from the reaction flask. The silver salts were filtered off and the reaction flask was washed with 20 mls of dichloromethane. The combined filtrates were washed with sodium chloride and water. The organic layer was dried and concentrated to give a light yellow viscous liquid. The ν_{C-Br} had vanished from the i.r., but no discernable ν_{C-F} peak had appeared. The mass spectrum of the product had many peaks in excess of 200, but there was no peak at 126 (the mass of 1-fluro-1-phenylethane). V.p.c. analysis on SE-30 gave only one peak, close to that of ethyl benzene, and with a retention time much shorter than that of 1-bromo-1-phenylethane.

The attempted fluorination of 1-bromo-1-phenylethane using potassium fluoride

Anhydrous potassium fluoride (5.8 g, 0.01 mole) was stirred at 120-130° in 20 mls of N-methylpyrrolidone which had been dried over magnesium sulphate and distilled (202-3°). The 50 ml reaction flask was fitted with a two-arm adapter which held a thermometer and dropping funnel. 1-Bromo-1-phenylethane (1.85 g, 0.01 mole) in N-methyl-pyrrolidone (10 mls) was added over 4 hours. When addition was complete, the temperature was increased to 180° and maintained there for a further 4 hours. At this temperature the thermometer was replaced by a cold-finger. The produce was extracted by taking the dark reaction mixture up in dichloromethane and water and washing successively with water, saturated ammonium chloride solution (4 x 150 mls), and water. After drying over magnesium sulphate the organic layer was concentrated to yield only 0.41 g of dark product. This product had spectral properties similar to the product obtained when silver fluoride was used as the catalyst. These indicated that the desired reaction did not take place.

The attempted fluorination of 3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**) using sulphur tetrafluoride

All reactions were carried out in a 25 ml autoclave which was charged through a monel gas line. The volatile reagents (SF_4 : b.p. -40°; BF_3 : b.p. -127°) were distilled from commercial gas bottles into traps in the line, and thence redistilled into the autoclave. Sulphur tetrafluoride was not difficult to transfer, but the more volatile boron trifluoride required careful handling, because too much pressure tended to be built up in the line if the distilling trap was warmed too quickly. In each run 0.5 g (2.5 mmole) of the ketone and about 10 mls (0.1 mole) of sulphur tetrafluoride were used. Four reactions were carried out: the first at room temperature (20°) for four days; the second at room temperature in the presence of boron trifluoride (1 ml) for four days; the third at 150° with a catalytic 5 mls of anhydrous hydrogen fluoride for 12 hours; and finally with stirring in 2 mls of dichloromethane and 4 mls of boron trifluoride for fourteen days at 35-40°. Reactions were worked up by evaporation of the low boiling reactants and taking the product up in benzene-ether. The organic layer was washed with water, bicarbonate solution, and water. After drying over magnesium sulphate the solvents were evaporated.

Only starting material was recovered from the first two reactions at room temperature. The products of the latter two reactions were non-volatile, charred solids. They bore no evidence (i.r., v.p.c.) of containing either the starting material or fluorinated hydrocarbon.

The Nitro-acetoxylation of Carbocyclic Aromatics

Purification of nitric acid: To fuming nitric acid (300 mls) was added urea (10 g) and air was bubbled through the solution for 45 minutes, until it was colourless. The solution was cooled to 0° and concentrated sulphuric acid (500 mls) was added. From time to time samples of fuming nitric acid were distilled (20°/15 or 1 mm) from this magnetically stirred solution through a vigreux column into a trap at -180°. The samples were stored in a refrigerator at -5°.

The nitro-acetoxylation of indan (**64**) at low temperatures

Indan (11.8 g, 0.1 mole) was added to acetic anhydride (25 mls) and the solution was cooled to -78°. To the cooled solution was added a solution, also at -78°, of fuming nitric acid (7.5 g, 5 mls, 0.12 moles) in acetic anhydride (25 mls) which had been mixed previously at -10 to 0°. The reaction mixture was then allowed to warm to c.a. -35° and was stirred at this temperature for one hour before being

poured into carbon tetrachloride (400 mls) which had been cooled to -15° by dropping dry ice into it. It was necessary to ensure that all the solid carbon dioxide had been dissipated before the addition of the reaction mixture was made. The carbon tetrachloride solution was washed twice with 400 mls each of water, 2% aqueous ammonia solution, and water. The second ammonia washing retained its basicity and assumed a pale yellow colour. The first washing was weakly acidic and colourless. The organic layer was dried over magnesium sulphate and rotary evaporated at room temperature to yield 18.6 g of a pale green liquid: i.r. (film) 1735 (ester C=O), 1545 (aliphatic $C-NO_2$), 1520 (aromatic $C-NO_2$), 1230 cm^{-1} (C-OAc); n.m.r. (CCl_4) τ 1.9-3.3 (61%, aromatic protons), 3.5-4.6 (39%, vinylic and allylic protons), 7.93 and 8.02 p.p.m. (relative heights: 1:3, CH_3CO_2). N.m.r. also indicated that all the indan had reacted. When the crude product was stood overnight in an ice-box colourless crystals formed. These were filtered off and recrystallized twice by dissolving them in approximately fifty times their weight of boiling pentane and reducing this volume to about a third, or until crystals started to form, and cooling to 0°. This procedure was repeated twice until 3.2 g of a nitro-acetoxy adduct of indan had been collected:

cis-5-Acetoxy-5,7a-dihydro-7a-nitroindan (**67**): m.p. 60-61°; i.r. (Nujol) 1735 (ester C=O), 1545 (aliphatic C-NO_2), 1230 cm^{-1} (C-OAc); u.v. max. (95% C_2H_5OH), 203 nm (ε 970 m^2 mol^{-1}); n.m.r. (CCl_4) τ 3.53 and 3.70 (nq, 1, J_{67}^{APP} = 10 Hz, H_7), 3.77, 3.80, 3.84, 3.86, 3.97, and 4.00 (nq, 1, J_{67}^{APP} = 10 Hz, J_{56}^{APP} = 3.9 Hz, J_{46}^{APP} = 1.5 Hz, H_6), 4.0 (b, 1, H_4), 4.39, 4.44, 4.47, and 4.53 (m, 1, J_{45}^{APP} = 5.0 Hz, J_{56}^{APP} = 3.8 Hz, H_5) 7.98 p.p.m. (s, 3, $OCOCH_3$). Samples sent for elemental analysis and precise mass spectral measurement decomposed in transit.

The fourth crop from the recrystallization of the crude product was the nuclear substituted nitro compound:

5-Nitroindan: m.p. = 36.0-37.5° (cf 40.0-.5[110]); i.r. (melt) 1590 (aromatic ring), 1510, 1345 cm^{-1} (aromatic C-NO_2); n.m.r. (CCl_4) τ 2.0-2.25 (m, 2, H_4 and H_6), 2.65-2.9 (m, 1, H_7), 6.8-7.2 (m, 4, benzylic H), 7.6-8.3 p.p.m. (m, 2, aliphatic H).

When the mother liquor from recrystallization was analyzed by n.m.r. spectroscopy an enrichment, compared with the spectrum of the crude reaction mixture, was observed for minor peaks in the dienic region of the spectrum. These peaks showed similar splitting relationships to those of the adduct **67**.

The nitro-acetoxylation of tetralin (**65**)

Tetralin (13.2 g, 0.1 mole) in acetic anhydride (25 mls) was frozen at -78° and treated with a solution of fuming nitric acid (9.0 g, 6 mls, 0.15 mole) in acetic anhydride (25 mls). The mixture was allowed to warm to 0° and it was stirred between 0 and 3° for 10 hours before being stood overnight in a refrigerator at -5°. The product was extracted by the method used for indan and yielded 18.1 g of a reddish gum: i.r. (smear) 1735 (ester C=O), 1545 (aliphatic C-NO_2), 1520 cm^{-1} (aromatic C-NO_2); n.m.r. (CCl_4) indicated that all the tetralin had reacted, and that the product was 50% diene. All attempts to induce crystallization using various solvents at low temperatures were unsuccessful. A sample of diene was isolated by dissolving 1.0 g of the product in 10 mls of 1:10 ether-pentane and columning it on 10 g of basic alumina (deactivated 5% with water, 11 x 110 mm). The column was eluted with 40 mls each of pentane, 1:20 and 1:10 ether-pentane, and ether. The elution was carried out using reduced pressure in a total time of 10 minutes. Pentane brought through 0.38 g of solely aromatic nitro compound (ν_{C-NO_2} = 1520 cm^{-1}), followed by 0.2 g of diene contaminated with small amounts of aromatic acetoxy compound ($\nu_{C=O}$ = 1765 cm^{-1}) and aromatic nitro compound. 1:10 ether-pentane eluted pure diene:

cis-7-Acetoxy-4a,7-dihydro-4a-nitrotetralin: i.r. 1735 (ester C=O), 1545 cm^{-1} (aliphatic C-NO_2); n.m.r. (CCl_4) τ 4.03 (s, 2, H_5 and H_6), 4.16 (m, 1, H_6), 4.36 (m, 1, H_7), 7.2 (m, 1, $H_{1\alpha}$) 7.65 (m, 2, $H_{2\alpha}$ and $H_{3\alpha}$), 7.98 (s, 3, CH_3CO_2), 8.0-9.0 p.p.m. (m, 5, $H_{4\alpha}$, $H_{1\beta}$, $H_{2\beta}$, $H_{3\beta}$, and $H_{4\beta}$).

The nitro-acetoxylation of benzsuberan (**66**)

Benzsuberan (3.0 g, 0.02 mole, produced from the Clemmensen reduction of benzsuberone) was mixed with acetic anhydride and cooled to -78°. To the frozen mixture was added a solution of fuming nitric acid (1.2 mls, 1.8 g, 0.03 mole) in acetic anhydride (10 mls), also at -78°. The temperature was allowed to rise to -20°, by which time the reaction medium was homogeneous. The solution was stirred at -20° for two hours, during which time a solid precipitated out. The product was extracted in a manner similar to that used for the nitro-acetoxylation of indan. Only 1.8 g, or less than half of the expected quantity, of the product was obtained, because the magnetic stirring bar went through the bottom of the reaction flask. The diene adduct decomposed before it could be separated from the remainder of the products. Some spectral analyses were made before decomposition: i.r. (film) 1740 (ester C=O), 1545 (aliphatic C-NO_2), 1520 cm^{-1} (aromatic C-NO_2); n.m.r. (CCl_4) τ 1.9-3.0 (57% of product by comparison with integral

of diene-allylic region, aromatic H), 3.7-4.5 (43%, diene and allylic H), 7.98 and 8.03 p.p.m. (relative heights 22:13, CH_3CO_2).

The reaction of 3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**) with fuming nitric acid and acetic anhydride.

The tricyclic ketone **14** (10 g, 0.05 mole) was stirred heterogeneously with acetic anhydride (25 mls) at -78°. A solution of nitric acid in acetic anhydride was prepared by adding dropwise fuming nitric acid (7.5 g, 5.0 mls, 0.12 mole) to acetic anhydride (25 mls) at a temperature less than -50°. This solution was then added slowly to the ketone-anhydride mixture such that the temperature did not exceed -50°. The reaction mixture was then allowed to warm to 0°. At -20° the colour of the reaction changed from fawn to mauve, and at -10° dissolution was complete. Some minutes later when the reaction had reached 0°, a solid started to form. The reaction mixture was stirred for a further 3 hours at 0±5°, by which time the original fawn colour had returned. The products were extracted by pouring the reaction mixture into carbon tetrachloride (400 mls) which had been cooled by dropping dry ice into it. The carbon tetrachloride solution was washed with water (3 x 400 mls), 2% aqueous ammonium hydroxide (2 x 400 mls), and water. After drying over

magnesium sulphate the solvent was evaporated at room temperature. The residue weighed 18.6 g: i.r. (film) 1735 (aliphatic ester C=O), 1705-1675 (ketone C=O), 1545-1520 cm^{-1} ($C-NO_2$); n.m.r. ($CDCl_3$) τ 1.3-3.0 (61% allowing for 2 aromatic protons), 3.5-4.1 (39% allowing for 3 dienic and allylic protons). V.p.c. analysis of the products on QF-1 and SE-30 columns gave only four peaks. A 5 ft. 15% QF-1 on VP-30 column at 250° gave the following percentages of aromatic compounds in the product: 5 minutes from injection, 1%, ketone **14**; 18.4 mins., 1%, 6-isomer; 42 mins., 34%, 5-isomer; 58.4 mins., 26%, 4-isomer. These percentages were calculated from the v.p.c. trace in conjunction with the 3:2 ratio of aromatic compounds to dienes indicated by the n.m.r., as no diene or their aromatic acetoxy decomposition products were detected by v.p.c.

The separation of five products and the starting material was achieved by recrystallization, chromatography, and further recrystallization. The crude product was initially separated into five fractions by recrystallization. The first fraction, the precipitate obtained by recrystallizing the product from 20 mls of carbon tetrachloride, weighed 5.45 g and i.r. suggested that it was mainly aromatic nitro compound. The second precipitate, 1.36 g, was obtained by recrystallizing the concentrated mother liquor of the first recrystallization from 5 mls of carbon tetrachloride. It was found to be mainly diene, as were all the following

fractions. The third precipitate, 3.74 g, was obtained from 10 mls of 1:1 benzene-pentane, and the fourth, 0.7 g, from 10 mls of 1:3 benzene-pentane. The fifth fraction, 0.8 g, was the concentrate of the mother liquor of the fourth recrystallization.

The components of the first recrystallization fraction were separated by further recrystallization. 125 mls of hot methanol were required to dissolve all the solid . On cooling, all the diene component remained in the mother liquor. The nitro compounds (4.0 g) were recrystallized twice from 200 mls of methanol. The precipitate (1.45 g) was recrystallized a further two times from 80 mls of ethanol to yield 0.8 g of pale yellow needles: m.p. 149.5-9.8°. These were found to be the 5-nitro isomer **71**. The mother liquor from the second methanolic recrystallization was concentrated (1.8 g) and recrystallized five times from 30 to 20 mls of ethanol until only a single crystal form was obtained: m.p. 124.5-5.1°. This was found to be the 4-nitro isomer **70**. Analytical samples of the 4- and 5-isomers were obtained by subliming their crystals at 120° and 145° respectively at 0.002 mm.

4-Nitro-3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de] naphthalene (**70**)

This compound formed white bipyramidal octahedrons

from ethanol: m.p. 124.5-5.1°; i.r. (Nujol) 1705 (C=O), 1595 (aromatic ring), 1535 cm^{-1} (aromatic C-NO_2); u.v. max. (95% C_2H_5OH) 215 (ε 1,900), 254 (shoulder, ε 650), 304 (ε 250 m^2 mol^{-1}); n.m.r. ($CDCl_3$) τ 2.62 and 2.86 (2, q, J = 8 Hz, H_5 and H_6), 6.8 (1, m, C_6H_2CH), 7.1 (2, m, $C_6H_2CH_2$), 7.4 (2, m, $COCH_2$), 7.5-9.0 p.p.m. (8, m, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 245.1048 (53, M_r ($^{12}C_{14}{}^{1}H_{15}{}^{14}N{}^{16}O_3$) = 245.1052), 229 (3), 217 (35), 201 (28), 187 (14), 184 (14), 173 (13), 171 (13), 161 (13), 159 (19), 143 (29), 141 (37), 129 (44), 128 (100), 127 (39), 115 (86), 91 (32), 77 (33).

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.93; H, 6.15; N, 5.73.

5-Nitro-3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de] naphthalene (**71**).

This compound formed pale yellow needles from ethanol: m.p. 149.5-9.8°; i.r. (Nujol) 1695 (C=O), 1605, 1590 (aromatic ring), 1520 cm^{-1} (aromatic C-NO_2); u.v. max. (95% C_2H_5OH) 202 (ε 1,640), 242 (ε 2,980), 274 (ε 1,180), 320 (shoulder, ε 360 m^2 mol^{-1}); n.m.r. ($CDCl_3$) τ 1.42 and 1.93 (2, q, J = 2.5 Hz, H_4 and H_6), 6.7 (1, m, C_6H_2CH), 7.0 (2, m, $C_6H_2CH_2$), 7.3 (2, m, $COCH_2$), 7.5-9.0 p.p.m. (8, m, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 245.1060 (100, M_r ($^{12}C_{14}{}^{1}H_{15}{}^{14}N{}^{16}O_3$) = 245.1052), 228 (20), 217 (17), 203 (34), 199 (39), 189 (10), 188 (9),

171 (16), 142 (17), 141 (26), 129 (38), 128 (55), 127 (22), 115 (47), 91 (14), 87 (20).

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.44; H, 6.15; N, 5.75.

The second recrystallization fraction was subjected to solid-liquid chromatography in order to separate the dienes from the nitro compounds. The dienes were found to be stable enough to withstand normal columning techniques. 1.32 g of solid were dissolved in 5 mls of benzene and placed on 50 g (300 x 15 mm) of 7½% aqueous deactivated neutral alumina. The first five 50 ml column lengths (pentane; 10%, 20%, 50% (2x) benzene-pentane) all contained some amount of aromatic nitro compound. The sixth to ninth column lengths (1:1 benzene-pentane (2x), benzene (2x)) concentrated to 0.65 g and contained only diene.

trans-4-Acetoxy-6a-nitro-1,2,3,4,6a,7,8,9,10,10a-decahydrocyclohepta[de]naphthalene (**68**)

The concentrate of the sixth to ninth column lengths was recrystallized from benzene (3x) and ether to give white cubic crystals: m.p. 120.5° (with decomposition); i.r. (Nujol) 1735 (ester C=O), 1690 (tetra substituted and conjugated C=C), 1675 (conjugated C=O), 1640 (C=C), 1545 cm^{-1} (C-NO_2); u.v. max. (95% C_2H_5OH) 204.5 (ε 690), 241.5 (ε 810 m^2 mol^{-1}); n.m.r. ($CDCl_3$) τ 3.47, 3.54, 3.63, and 3.70 (1, J_{56}^{APP} = 9.5 Hz, J_{45}^{APP} = 4 Hz, H_5), 3.80 and 3.87 (1,

J_{45}^{APP} = 4 Hz, H_4), 3.84 and 4.00 (1, J_{56}^{APP} = 9.5 Hz, H_6), 8.01 (3, s, OCOCH_3), 7.0-9.3 p.p.m. (alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 259.1340 (<1, M_r ($^{12}C_{16}{}^{1}H_{19}{}^{16}O_3$) = 259.1334, = $M^{\dagger} - NO_2$), 245.1051 (5, M_r ($^{12}C_{14}{}^{1}H_{15}{}^{14}N{}^{16}O_3$) = 245.1052, = $M^{\dagger}$ - HOAc), 217 (5), 216 (4), 201 (11), 200 (65), 185 (6), 172 (13), 159 (22), 158 (100), 144 (18), 143 (30), 141 (10), 130 (20), 121 (39), 129 (30), 115 (33).

Anal. Calcd. for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 62.74; H, 6.23; N, 4.56.

The third initial recrystallization fraction was also chromatographed in order to separate diene from aromatic nitro compound. 2.0 g were dissolved in 5 mls of benzene and placed on 50 g (300 x 15 mm) of 7½% aqueous deactivated neutral alumina. The diene was difficult to separate from the aromatic nitro compound which trailed through the column and was not completely eluted until 4 x 50 mls of 1:1 benzene-pentane had been used as eluant. 2 x 50 mls of benzene eluted 0.46 g of diene. This was recrystallized five times from 4 to 1 ml of 1:1 benzene-pentane, and was characterised as the diene **69**.

cis-4-Acetoxy-6a-nitro-1,2,3,4,6a,7,8,9,10,10a-decahydro-cyclohepta[de]naphthalene (**69**)

This diene crystallized from 1:1 benzene-pentane to give white prisms: m.p. 104.0-4.8° (with decomposition);

i.r. (Nujol) 1735 (ester C=O), 1680 (tetrasubstituted and conjugated C=C), 1675 (conjugated C=O), 1635 (C=C), 1545 cm^{-1} (C-NO_2); u.v. max. (C_2H_5OH) 205.5 (ε 710), 241 (ε 830 m^2 mol^{-1}); n.m.r. ($CDCl_3$) τ 3.63, 3.68, 3.80, and 3.85 (1, J_{56}^{APP} = 10 Hz, J_{45}^{APP} = 3 Hz, H_5) 3.87 and 3.91 (1, J_{45}^{APP} = 3 Hz, J_{46}^{APP} = 0.75 Hz, H_4) 3.93 and 4.10 (1, J_{56}^{APP} = 10 Hz, J_{46}^{APP} = 0.75 Hz, H_6), 7.98 (3, s, OCOCH_3), 7.0-9.2 p.p.m. (alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 259.1328 (4, M_r ($^{12}C_{16}{}^{1}H_{19}{}^{16}O_3$) = 259.1334, = $M^{\dagger}$ - NO_2), 245.1058 (10, M_r ($^{12}C_{14}{}^{1}H_{15}{}^{14}N{}^{16}O_3$) = 245.1052, = $M^{\dagger}$ - HOAc), 233 (6), 217 (55), 216 (95), 201 (23), 200 (97), 185 (19), 172 (28), 159 (42), 158 (100), 144 (35), 143 (55), 141 (24), 130 (40), 129 (79), 128 (63), 115 (74).

Anal. Calcd. for $C_{16}H_{19}NO_5$: C, 62.94; H, 6.27; N, 4.59. Found: C, 63.11; H, 6.28; N, 4.53.

The fourth recrystallization fraction was found to be an even mixture of diene and aromatic nitro compound and no attempt was made to purify it further. The mother liquor from the fourth recrystallization was concentrated (0.8 g) and taken up in 4 mls of 1:1 benzene-pentane and columned on 50 g (300 x 15 mm) of 7½% aqueous deactivated neutral alumina. The column was eluted with 50 mls of pentane, 1:10 benzene-pentane (2x), and 1:5 benzene-pentane (2x) before 1:1 benzene-pentane brought down 0.12 g of unreacted ketone **14**. The seventh column length, also 1:1

benzene-pentane, eluted 0.16 g of the aromatic nitro compound **72**. A further two column lengths of 1:1 benzene-pentane and one of benzene eluted 0.13 g of the nitro isomer **70**. A final elution with benzene (2 x 50 mls) brought down 0.13 g of the diene **69**.

6-Nitro-3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[de] naphthalene (**72**).

The concentrate of the sixth column eluant was recrystallized from ethanol-chloroform and ethanol (2x) and then sublimed at 65°/0.002 mm: m.p. 68.0-69.8°; i.r. (Nujol) 1695 (C=O), 1595 (aromatic ring), 1530 cm^{-1} (aromatic C-NO_2); u.v. max. (95% C_2H_5OH) 213 (ε 1,870), 252.5 (ε 930), 307 (ε 240 m^2 mol^{-1}); n.m.r. ($CDCl_3$) τ 2.0 and 2.57 (2, q, J = 8.5 Hz, H_4 and H_5), 6.7 (1, m, C_6H_2CH), 7.0 (2, m, $C_6H_2CH_2$), 7.4 (2, m, $COCH_2$), 7.5-9.0 p.p.m. (8, m, alicyclic CH_2); mass spectrum (70 eV) *m/e* (relative intensity) 245.1060 (59, M_r ($^{12}C_{14}{}^{1}H_{15}{}^{14}N^{16}O_3$) = 245.1052), 229 (31), 228 (100), 210 (14), 200 (40), 199 (20), 172 (18), 170 (16), 158 (25), 141 (42), 129 (40), 128 (65), 127 (33), 115 (87), 91 (34), 89 (24), 77 (46), 55 (55), 39 (56).

Anal. Calcd. for $C_{14}H_{15}NO_3$: C, 68.55; H, 6.16; N, 5.71. Found: C, 68.64; H, 6.14; N, 5.70.

The nitro-acetoxylation of 5,6,7,8-tetrahydrocyclohepta[*fg*] acenaphthene (**57**)

1. At -20° to +20° in an n.m.r. tube: The cyclo-heptaacenaphthene **57** (50 mgm) was dissolved in 0.4 mls of $CDCl_3$ and frozen in an n.m.r. tube at -180°. To this was added a few drops of nitric acid-acetic anhydride solutions and the tube was then allowed to warm in the n.m.r. spectrometer. The n.m.r. machine could not be locked onto signal from the methyl groups of the acetic anhydride until the temperature had risen to -20°, owing to the plug of frozen hydrocarbon in the tube not having thawed to allow mixing of the two solutions. When mixing did occur, the diene region [200 to 290 Hz downfield from $(CH_3CO)_2O$] gave an integral ratio to the aromatic region [290 to 370 c.p.s. downfield from $(CH_3CO)_2O$] which indicated that the reaction mixture was c.a. 50% diene adduct. The n.m.r. tube was allowed to warm to +5°, and little change was observed in the integral ratio. However, when isolation of the adduct was attempted using the extraction technique which was used for indan, no diene was detected (i.r., n.m.r.) in the products.

2. At -25°: The cycloheptaacenaphthene **57** (416 mgm, 2 mmoles) was dissolved in 12 mls of anhydrous methylenechloride and treated at -78° with 0.17 mls (252 mgm, 4 mmoles) of fuming nitric acid in 2 mls of acetic anhydride.

The frozen mixture was allowed to warm to -25°, and was stirred between -25 and -30° for half an hour before being poured into 80 mls of super-cooled methylene chloride. Isolation of the products followed the technique used for indane, and yielded 405 mgm of a yellow solid. I.r. and n.m.r. analyses indicated the absence of any nitro-acetoxy adduct, but the presence of an aliphatic nitro group. When the product was recrystallized twice from carbon tetrachloride a sharp melting light yellow solid was obtained:

1-Nitro-5,6,7,8-tetrahydrocyclohepta[fg]acenaphthene (**74**): m.p. 123.0-3.7°; i.r. (Nujol) 1595 (aromatic ring) 1555 (aliphatic C-NO_2) 835, 826, 792 cm^{-1} (aromatic C-H bending); n.m.r. (CCl_4) τ 2.43 and 2.55, 2.72 and 2.84 (q, 2, J^{APP}_{910} = 7 Hz, J^{APP}_{110} = 1.0 Hz, H_{10} and H_9 respectively), 2.82 (s, 2, H_3 and H_4), 3.65, 3.67, 3.74, and 3.79 (q, 1, $J^{APP}_{12\alpha}$ = 7.5 Hz, $J^{APP}_{12\beta}$ = 3.0 Hz, H_1) 5.70, 5.75, 6.00, and 6.05, and 6.11, 6.23, 6.41, and 6.53 (octet, 2, $J^{APP}_{2\alpha 2\beta}$ = 18 Hz, $J^{APP}_{12\alpha}$ = 7.5 Hz, $J^{APP}_{12\beta}$ = 3.0 Hz, $H_{2\beta}$ and $H_{2\alpha}$ respectively), 6.80 (b, 4, H_5's and H_8's), 7.85-8.05 p.p.m. (m, 4, H_6's and H_7's); mass spectrum (70 eV) *m/e* (relative intensity) 253 (6, M_r ($^{12}C_{16}{}^{1}H_{15}{}^{14}N^{16}O_2$) = 253), 237 (1), 221 (2), 208 (18), 207 (100), 191 (8), 189 (9), 179 (9), 178 (8), 165 (33).

This compound was photosensitive and it decomposed before it was analysed for its elemental composition.

3. At -78°: The cycloheptaacenaphthene **57** (208 mgm, 1 mmole) was dissolved in 1 ml of anhydrous chloroform and frozen at -78°. It was then treated with 0.2 mls (0.3 g, 5 mmoles) of fuming nitric acid in 1 ml of acetic anhydride. The heterogeneous reaction mixture was stirred for six hours at -78° before it was neutralised at this temperature with gaseous ammonia. The excess ammonia was then pumped off. To ensure complete removal of the ammonia it was found that the solvent also had to be evaporated. The residue was taken up in water-dichloromethane and washed with water. The organic layer was dried and evaporated: i.r. (smear) 1735 (ester C=O), 1550 (aliphatic C-NO_2), 1530 (aromatic C-NO_2), 1230 cm^{-1} (C-OAc). The n.m.r. spectrum of the product indicated that diene was present in the mixture as there were peaks in the diene region (3.3-4.5 τ). The diene, presumed to be of the structure **73**, could not be isolated from the other products without its decomposing.

The nitro-acetoxylation of 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*]naphthalene (**17**)

1. N.m.r. *in situ* study of the reaction: The hydrocarbon (40 mgm) was dissolved in $CDCl_3$ (0.4 ml) and frozen at -180°. To this was added excess nitric acid-acetic anhydride mixture and the solid was allowed to thaw slowly. Frequencies in the diene region were observed at

-30° and persisted even at room temperature. The product was worked up in the usual aqueous ammonia washing manner to yield 37 mgms: i.r. (smear) 1745 (ester C=O), 1555 (aliphatic C-NO_2), 1235 cm^{-1} (C-OAc).

2. At -35°: The hydrocarbon (59 mgm, 0.25 mmole) was frozen at -78° with acetic anhydride (5 mls) and treated with a mixture of nitric acid (1 ml, 1.5 g, 25 mmole) and acetic anhydride (5 mls). The mixture was allowed to warm to -35°, and it was then stirred at -35 to -40° for half an hour. The reaction was quenched by pouring it into 50 mls of CCl_4 and washing it twice each with 160 mls of water, 2% aqueous ammonia, and water. The organic layer was dried and concentrated: i.r. (smear) 1745 (ester C=O), 1550 (aliphatic C-NO_2), 1530 (aromatic C-NO_2), and 1235 cm^{-1} (C-OAc); n.m.r. (CCl_4) τ 2.60, 2.64, 2.75, 2.81, 2.97, and 7.08 (aromatic H), 3.54, 3.57, 3.71, and 3.75 (q, of minor integral), 4.00, 4.16, 4.17, and 4.33 (q, integral = 0.5 of aromatic region, J_{56}^{APP} = 9.5 Hz, H_5 and H_6), 6.5-8.8 (benzylic and alicyclic H), 8.00, 8.04, and 8.05 p.p.m. (probably two or all three from CH_3CO_2). The diene, which was presumed to be of the structure **75**, could not be isolated from the other products without it decomposing.

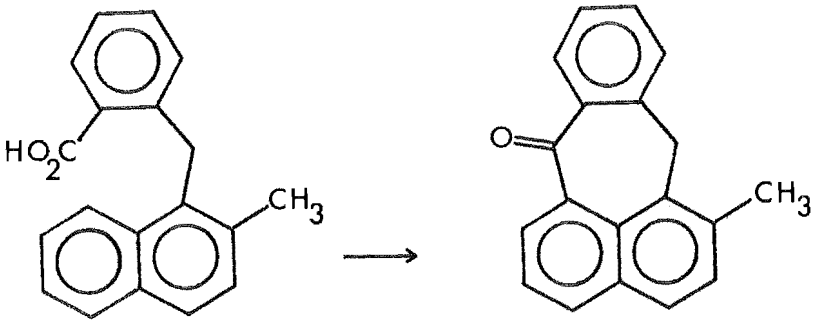
DISCUSSION

The Synthesis of 5,6,7,8-Tetrahydrocyclohepta[*de*]naphthalene (**5**)

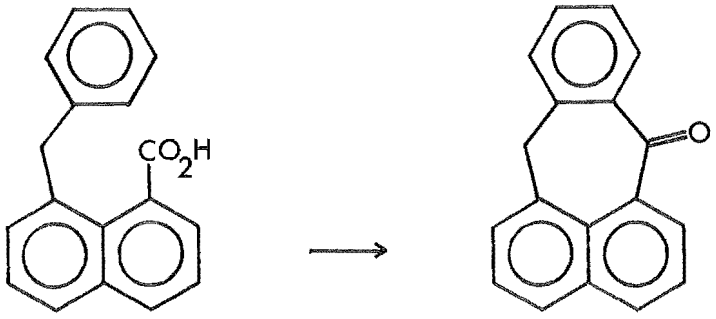
The successful synthesis gave **5** in a 44% yield from benzsuberone (see page 47) and with refinement this could be improved significantly. This would suggest that this route is superior to that of Gilmore and Horton[46] which gave pleiadane in a 35% yield from α-tetralone. This would be the case if it were not for the expense of benzsuberone (e.g. Aldrich: $14.50 for 5 g cf $50.00 for 500 g of α-tetralone). The 29% yield and ten-step synthesis from crotonaldehyde (an inexpensive precursor to benzsuberone) make this route less favourable.

The unsuccessful attempts to synthesis **5** which started with fully aromatised naphthalene derivatives both illustrate the difficulty of forming a seven-membered *peri*-substituted cyclic naphthalene. In the case of the proposed double Dieckmann condensation of dimethylnaphthalate **3** and diethylsuccinate the product diketodiester **4** would be more rigid and strained than the wholly alicyclic diketodiester which was formed from the condensation of dimethylglutarate and diethylsuccinate[65]. Furthermore, it would appear that the interior angles of the seven-membered ring of the product **4** make the formation of this compound by *peri*-cyclization unfavourable. Two examples of compounds which have undergone

cyclization to give seven-membered rings containing angles other than the tetrahedral angle are 2-(2'-methyl-1'-naphthylmethyl)benzoic acid[2] (**78**) and 8-benzyl-1-naphthoic acid[12] (**80**). Both these acids cyclized with ease, but when the



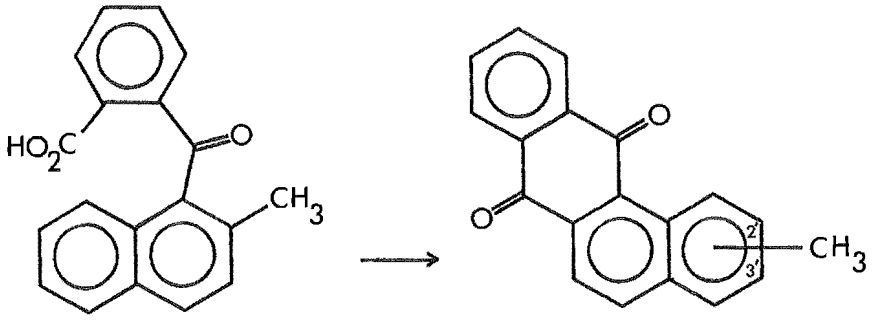
78 **79**



80

oxo derivative of **78**, 2-(2'-methyl-1'-naphthoyl)benzoic acid (**81**) was reacted under similar conditions no reaction occurred[111]. When conditions were made more severe cyclization resulted only subsequent to migration of the phthalic acid residue to the unsubstituted ring, upon which the

formation of 2'-methyl- and 3'-methyl-1,2-benzanthraquinones (**82**) occurred[112].



81 **82**

(The desired pleiadenedione which would have resulted from *peri* closure was, however, obtained from the oxidation of the pleiadenone **79**[2].) It is apparent, then, that for the formation of seven-membered *peri* cycles containing trigonal angles in the bridge, closure is favoured when the bridge carbons in the product enclose three trigonal angles. An exception to this generalisation is the formation of 5,8-dioxo-5,6,7,8-tetrahydro[*fg*]acenaphthene (**56**), but this is a special case and it will be discussed later.

Another factor which would inhibit the formation by cyclization of 5,8-dioxocycloheptanaphthalenes would be repulsion between the carbonyl dipoles. Electrostatic repulsion of this type is thought to be a contributing factor to the existence of 1,3-cyclohexanediones in largely their

enolic form[122]. The relative orientation of the carbonyl functions in the 5,8-dioxocycloheptanaphthalene **7** is similar to that found in 1,3-cyclohexanediones.

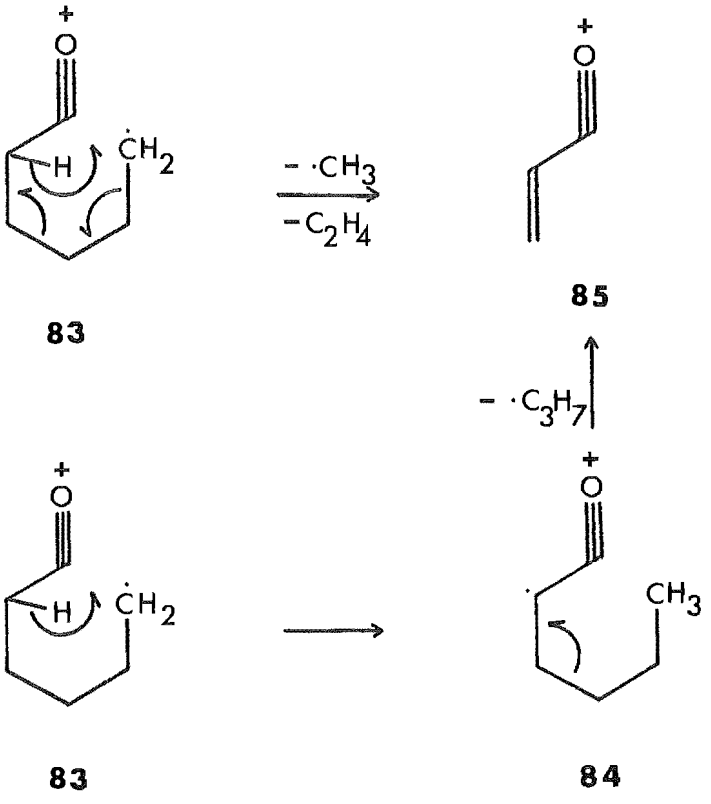
The failure of methyl 4-(1'-naphthalenyl)-4-oxobutanoate (**6a**) to cyclize is also in concurrence with the above generalisation. However, the naphthalene nucleus would be deactivated towards further electrophilic attack owing to the presence of the carbonyl function α to the ring, but this cannot be the only factor inhibiting cyclization because, for example, in the course of the formation of the methyl benzanthraquinones **82** the position of closure was α to the electron withdrawing group and therefore highly deactivated.

The attempted synthesis of pleiadane via 4-phenyloctandioc acid **11** (scheme I, page 44) was carried out only as a pilot run. The diester acid **9** had been prepared previously[96]. The hydrolysis-decarboxylation of **9** followed from the success of the reaction for the analogous compound **23a**. Unlike the reaction of **23a**, the hydrolysis-decarboxylation of **9** did not produce any lactone analogous to **25**, although the presence of lactone was detected ($\nu_{C=O}$ = 1770 cm^{-1}) in a sample withdrawn from the reaction after a short reflux period. It is curious that the product diacid **10** does not undergo "lacto-enoic tautomerism", for as will be seen in the discussion of the tautomerism of

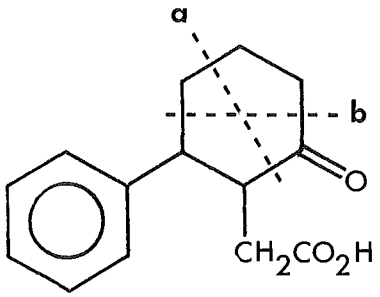
24 and **25**, the diacid is activated towards this type of tantomerism. The failure of the carboxylic acid functions of the diacid **11** to undergo simultaneous closure is undoubtedly due to the aromatic nucleus being deactivated towards further electrophilic attack after one carbonyl function has been substituted. Possibly a more reactive catalyst such as a melt of aluminium and sodium chlorides would have brought about closure, but the product would have been obtained in only a moderate yield.

The assignment of the structure 2-oxo-6-phenyl-cyclohexylacetic acid **76** to the solid melting at 129-131° isolated as a minor product from the reaction which gave the diacid **11** was made on the following basis: the infra-red spectrum indicates a carboxylic acid ($\nu_{C=O}$ = 1705, ν_{O-H} = 2700-2500 cm^{-1}), a carbonyl ($\nu_{C=O}$ = 1710 cm^{-1}), and a phenyl group ($\nu_{C-H\ bending}$ = 754 and 696 cm^{-1}). The u.v. spectrum of the compound (λ_{max} = 211, 259 nm; ε = 760, 22 $m^2\ mol^{-1}$ respectively) is consistent with a non-conjugated benzenoid. The λ_{max} of the compound's 2,4-dinitrophenyl-hydrazone is of slightly longer wavelength (365 nm, ε 2420 $m^2\ mol^{-1}$) than that for the derivative of the unsubstituted cyclohexanone (363 nm, ε 2350 $m^2\ mol^{-1}$ [122]), but this slight bathochromic shift may be the influence of a non-conjugated unsaturated function. For example, the dinitrophenylhydra-zine of methyl 2-methylpent-2-enyl ketone[113] has λ_{max} = 365

nm. The n.m.r. spectrum is complex but it gives the correct ratio of 1 : 5 : 10 for the acidic, aromatic, and aliphatic protons respectively. There are no chemical shifts unexpected for a compound of the suggested structure. The mass spectrum of **76** shows metastable peaks in agreement with the loss of phenyl, $\cdot CH_2CO_2H$, $\cdot CH_2CH_2CH_2CO\cdot$, and $CH_2{=}CH_2$ fragments. The cyclohexanone ring is characterised by fragmentation to give ions of *m/e* = 55 and 189. Cyclohexanone is known to fragment to *m/e* = 55[114]. It is suggested that the C-C bond α to the carbonyl function cleaves and the resulting ion **83** then undergoes further fragmentation by a concerted or stepwise (via **84**) mode to the ion **85**.



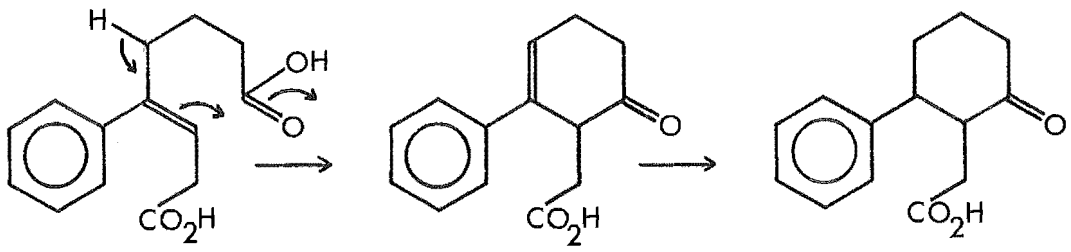
The compound **66** exhibits this type of fragmentation to give ions of *m/e* = 55 (**a**) and 189 (**b**) respectively.



66

The cleavages **a** and **b** provide evidence that the substitution pattern in the cyclohexanone ring is that shown. Any substitution pattern other than one α,β to the carbonyl function would give ions with *m/e* other than 55 and 189. Observations have been made on the effect of substitution in the cyclohexanone ring on the relative intensities of these cleavages[114], but these are of little value here as the larger ion would be prone to undergo further fragmentation. Further evidence for the given substitution pattern in the cyclohexanone ring is the loss of the $\cdot CH_2\text{-}CH_2\text{-}CH_2\text{-}C{\equiv}O\cdot$ radical to give the ion *m/e* = 162.

The formation of the cyclohexanone **66** probably results from acid-catalysed cyclization of the diacid **10** during the hydrolysis-decarboxylation step, and its subsequent reduction in the hydrogenation over palladium-on-carbon:



10 **66**

The Synthesis of 1,2,3,4,7,8,9,10-Octahydrodicyclohepta [*de*,*ij*]naphthalene (**17**)

The optimum overall yield for the synthesis of from cinnamaldehyde (**18**) was 6% (scheme II, page 48). This apparently low yield is the result of the length of the synthesis rather than poor-yielding steps, as most of the individual syntheses gave yields in the vicinity of 90%. The overall yield could be improved by the recycling of unreacted tricyclic ketone **14** recovered from the relatively low-yielding Reformatsky reaction. The yield of 68% for the synthesis of the acid **26** from benzsuberone (**22**) was a big improvement on Horton's[46] 11% yield, and a significant improvement on his later synthesis[44] via a Darzens reaction and subsequent malonate condensation which gave a yield of 43%.

Cook *et al* proposed the structure **23a** (with the double bond *endo*) for the product of the Stobbe condensation of benzsuberone, after they had reacted it with zinc chloride-acetic acid-acetic anhydride mixtures to give the benzo-azulene **39** . However, this evidence is not conclusive as under the vigorous acidic conditions an *exo* double bond could have isomerised to the *endo* position and the product could then have undergone cyclization to give the azulene derivative. That the *endo* isomer is the major product is shown by n.m.r. spectroscopy. From the ratio of the integrated intensity of the triplet at 3.95 which we attribute to the single olefinic proton of the *endo* isomer **23a** to that of the multiplet at 2.85 τ attributed to the aromatic protons of both **23a** and its *exo* isomer it may be calculated that the *exo* isomer could have constituted up to one-third of the mixture. Further confirmation that the predominant product is the *endo* olefinic half-ester was obtained by hydrolysis of the carbethoxy group and isolation of the *endo* olefinic diacid. The n.m.r. spectrum of the hydrolysis product, which shows a triplet at 3.8 which integrates for one proton, a multiplet at 5.96 τ (one proton), and a multiplet at 8.16 τ (two protons) establishes the *endo* diacid structure. The absorption at 3.8 τ is assigned to the vinylic proton split into a triplet by the adjacent methylenic protons. The absorption at 5.96 τ is assigned to the

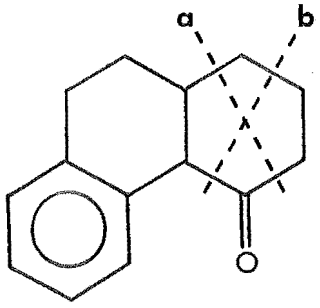
proton at C-2 which is both allylic and α to a carboxyl group. The absorption at 8.16 τ is attributed to an alicyclic methylene. The *exo* isomer has no vinylic protons. It has two protons both allylic and α to a carboxylgroup and has four alicyclic methylene protons. Although the *exo* isomer has the double bond α,β to a carbethoxy group which also brings the carbethoxy group into conjugation with the benzene ring, it is apparently less stable than the *endo* isomer which has the double bond β,γ to carbethoxy. Presumably the dominant factor is the greater relative stability of the seven-membered ring containing the *endo* double bond.

The main products from the hydrolysis-decarboxylation of the half-ester **23a** , the olefinic acid **24** and the lactone **25** , exhibited "lacto-enoic tautomerism" (see page 58). This was first described by Linstead and Rydon[115] who observed that when the double bond of an olefinic acid is suitably substituted it will undergo acid-catalysed tautomerism with its lactone. That the olefinic acid **24** , and not the olefinic acid **35** , was the product of the hydrolysis-decarboxylation reaction is a further indication that a seven-membered ring of this structural type prefers an *endo* double to an *exo* one. The *exo* bond in the olefinic acid **35** would be even less favoured than in the *exo* isomer of the half-ester **23a** because in the latter the double

bond would be stabilised by conjugation with the ester function.

The neutral compounds isolated after the reduction of the lactone **25** were identified as 1,2,3,4-tetrahydrophenanthrene (**36**), 1,2,3,4,4a,9,10,10a-octahydrophenanthrene (**38**), and 1,2,3,4,4a,9,10,10a-octahydro-4-oxophenanthrene (**37**). The oxophenanthrene **37** was characterised by its melting point and the melting point of its semicarbazone. Its spectral properties reinforce the assignment. The infrared spectrum of the compound suggests a 1,2 substituted benzo group (C-H bending for four adjacent aromatic hydrogens at 742 cm^{-1}) and a non-conjugated ketone (1710 cm^{-1}). The ultraviolet absorptions at 201 nm which broadens into a shoulder at 219 nm and at 267 nm are in the expected region for the primary and secondary bands of an *ortho* disubstituted methylenebenzene (o-xylene: 210[116] and 266 nm[123]). The band at the longest wavelength of the 2,4-dinitrophenylhydrazone of **37** (369 nm) was longer than that expected for a cyclohexanone derivative (363 nm), but it is shorter than that expected for the hydrazone of a conjugated ketone (377-379 nm[117]). The anomolously high wavelength for the hydrazone of **37** may be due to interaction between the π electron clouds of the benzene ring and the imine linkage, as these are held in close proximity, or to some other stereochemical property. For example, the 2,4-dinitrophenyl-

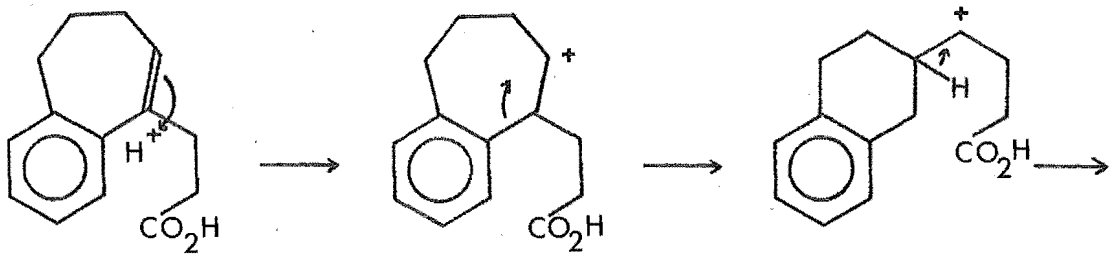
hydrazone of 5α-cholestane-3-one has λ_{max} at 370 nm[118]. The n.m.r. spectrum of **37** does not give conclusive evidence for the suggested structure, but it does give the required integral ratio of 4 : 12 for the ratio of aromatic protons to aliphatic protons. It also shows resonances within the expected frequencies for benzylic, α-keto, and alicyclic protons. The mass spectrum exhibits cleavages of the type seen in the cyclohexanone ring of **76**. The ion *m/e* = 157



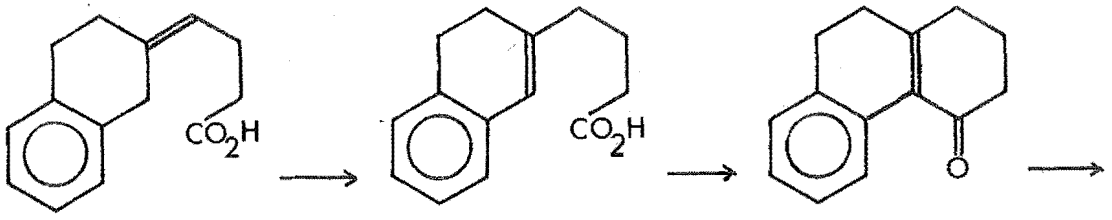
37

results from cleavage **a** and the ion *m/e* = 55 from cleavage **b**.

The oxophenanthrene **37** is probably formed by a skeletal rearrangement of the olefinic acid **24**, followed by acid catalysed cyclization and subsequent disproportionation (scheme VI).



24



85 86 87

37 88

38 36

SCHEME VI

The olefinic acid **24** undergoes anti-Markownikoff addition of a proton, followed by a skeletal rearrangement and proton loss to give the olefinic acid **85** . Although anti-Markownikoff addition is unfavoured, it is the only addition which will allow for subsequent skeletal rearrangement. The isomerisation of the olefinic acid **85** to **86** is favoured by an increase in mesomeric stabilisation energy. The cyclization of **86** to **87** is catalysed by the strongly acidic conditions under which the hydrolysis-decarboxylation of the half-ester **23a** is carried out. The olefinic ketone **87** ($M^{\dagger}$ = 198) was not detected in the product. This is because it would have been reduced to the ketone **37** and the octahydrophenanthrene **38** , or more probably, it underwent disproportionation to the ketones **37** and **88** . As will be seen later in the formation of the acids **43a** and **44a**, disproportionation occurs readily under acidic conditions in compounds of the structural type of **87**. The tetrahydrooxophenanthrene **88** ($M^{\dagger}$ = 196) was not detected in the product and it is assumed that this compound was reduced to the tetrahydrophenanthrene **36** .

1,2,3,4-Tetrahydrophenanthrene **36** was characterised by its melting point. The compound has the same molecular formula as pleiadane, but was found to differ spectrally. Its n.m.r. spectrum has the same aromatic:benzylic:alicyclic proton ratio (6:4:4) and characteristic dimethylene bridge

quintet (8.1 τ) as pleiadane but its resonance pattern varies in the aromatic and benzylic-type proton regions. Furthermore, the ultraviolet spectrum of **36** (C_2H_5OH: 233, 279.5, 321.5 nm cf 1,2,3,4-tetrahydrophenanthrene in cyclohexane: 230, 280, 322[119]) is distinctly different to that of pleiadane (C_2H_5OH: 232, 288, 323 nm) for the middle band which is characteristic of the substitution pattern in naphthalenes. The ultraviolet spectrum also eliminated the other two possible isomers: 1,2,3,4-tetrahydroanthracene (cyclohexane: 230, 276, 386 nm) and a cyclohexoazulene (e.g. 4,5-dimethylazulene in isooctane: 230, 284, 343 nm[120]). The assignment of the structure **36** to the above spectral data was substantiated by the aromatization of the compound to phenanthrene.

The by-product from the formation of the tricyclic ketone **14** was characterised by its melting point and the melting point of its semicarbazone as 4,5-benzo-1,2,3,6,7,8-hexahydro-1-oxoazulene (**39**), the compound obtained by Cook *et al*[69] from the cyclization of the half-ester **23a**. This assignment was confirmed by its infrared (conjugated C=O at 1685 cm^{-1}, four adjacent aromatic hydrogens bending at 735 cm^{-1}), ultraviolet (288 nm, 1930 $m^2\ mol^{-1}$ cf benzylidene acetone: 286 nm, 2500 $m^2\ mol^{-1}$ [121]), n.m.r. (integral ratio for aromatic to aliphatic protons is 4:10), and mass spectra (M^+ = 198). The formation of the oxoazulene **39** from the

cyclization of the olefinic acid **24** suggests that the acid **26** is contaminated with the olefinic acid when it is cyclized to **14** . This contamination could be the result of an incomplete hydrogenation of the olefinic acid **24** , or more probably, the acid **26** obtained from the reduction of the lactone **25** is contaminated with the olefinic acid **24** , owing to the lactone undergoing tautomerism in the acidic medium of the reduction. This tautomerism may also be responsible for the reduction of the lactone being incomplete, even after five hours of reflux. It is also possible that the olefinic acid **24** is produced from the saturated acid **26** during the cyclization of the latter. Polyphosphoric acid is known to dehydrogenate suitably activated molecules (e.g. the cycloheptaoxophenalene **45**), although while **26** is activated towards α,β-dehydrogenation it is not activated as much as the oxophenalene.

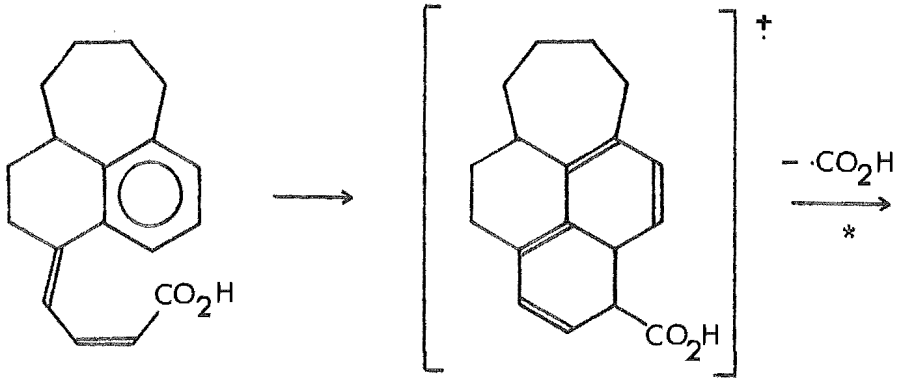
The formation of octahydrocycloheptanaphthalenylidene butanoic acid **28a** from the Reformatsky reaction and subsequent hydrolysis-hydration was the only unsatisfactory step in the synthesis, giving a yield of only 26% from the tricyclic ketone **14** . This step could be improved by performing a simple distillation at the end of the extraction procedure for the Reformatsky reaction, thus obtaining in one fraction the hydroxy ester **27** , some of which will have been thermally dehydrated to the diene ester **28b**,

and unreacted tricyclic ketone **14**. Treatment of this mixture with phosphorus oxychloride in pyridine would give a mixture of the diene ester and ketone only (this reaction was carried out and the yield was found to be quantitative), which could then be hydrogenated and hydrolysed to give the acid **29**, and the ketone **14** which would be isolated in the neutral fraction. Alternatively the diene ester-ketone mixture could be hydrogenated and cyclized directly, as esters in the presence of polyphosphoric acid cyclize as readily as their free acids, and the tricyclic and tetracyclic ketones could then be separated by fractional distillation. The compounds involved in the synthesis of the second seven-membered ring (**14**, **27** - **31**, **17**) were characterised by their mass spectra and their distinctive infrared $\nu_{C=O}$ or n.m.r. spectra. The spectral characteristics of dipleiadane bear many resemblances to those of pleiadane. The ultraviolet bands of longer wavelength have the same shape as those of pleiadane, but in general they are bathochromically shifted 11 nm. The n.m.r. spectrum shows the distinctive quintet of the dimethylene bridge protons at 8.04 τ and the broad benzylic proton resonances at 6.9 τ, similar to those of pleiadane, but with double the relative integral.

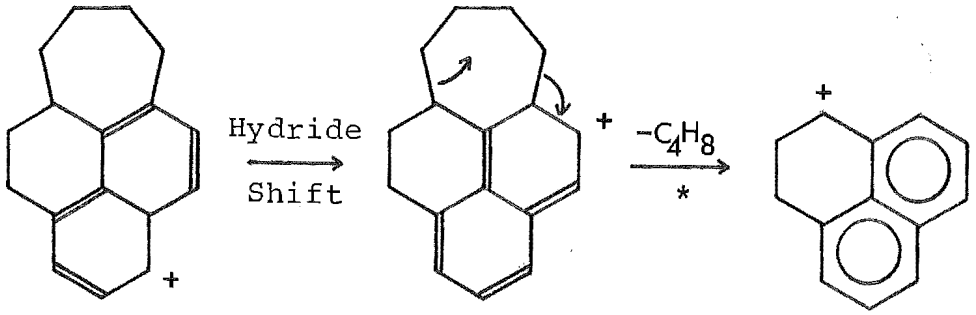
The mass spectra of the compounds of the synthesis exhibit many similarities and some interesting fragmentations. In the mass spectrum of the acid **26** and **29** the predominant

cleavage of the molecular ion is that in which the side chain is lost and a secondary cyclic carbonium ion, of mass 145 and 185 respectively and stabilized by the adjacent aromatic ring, is formed. A similar favoured cleavage to give a fragment of mass 143 occurs in the unsaturated acid **24** even though, formally, this would lead to a carbonium ion with the charge located on an unsaturated carbon atom. The lactone **25** also undergoes cleavage to generate an assumed similar carbonium ion of mass 143 and in this case a hydrogen atom is eliminated with the lactone "side chain". The spectra of acids **24** and **26** also show the loss of a fragment of mass 60. In the case of **24** this was demonstrated by precise mass measurement to be acetic acid and its formation may be explained as a McLafferty rearrangement product in which the charge remained with the larger (hydrocarbon) fragment. The predominant fission in the molecular ion of ketone **14** is that in which a fragment of mass 42 (ketene) is lost. Ketone **14** has the required substituent at the γ carbon atom[114]. Ketone **30** has a δ rather than a γ substituent and does not show a marked loss of mass 42 from the molecular ion. Loss of a mass 42 (C_3H_6) unit occurs from the molecular ion of hydrocarbon **31** . Fission of one of the seven-membered rings at a bond one removed from the benzene ring and at a second bond attached to the six-membered ring seems likely. A similar fission occurs in the fragment of

mass 185 in the spectrum of **29**. Loss of fragments of mass 42 also occurs from the ion of mass 183 in the spectrum of **30** and from the ion of mass 221 in the spectrum of **17**. Appropriate metastables were observed for all of the cited transitions. A proposed fragmentation of the unsaturated acid **28a** is depicted in scheme VII. The lower portion of the spectrum of **28a** is similar to that of the cyclohepta [*cd*]phenalene **49**.



28a



m/e = 223

m/e = 167

SCHEME VII

The Synthesis of 2,3,6,7,8,9-Hexahydro-1*H*-cyclohepta[*gh*] phenalene (**46**)

The 49% yield of the hydrocarbon **46** from the tricyclic ketone **14** reflects the efficiency of this synthesis (see scheme IV, page 64). However, this was achieved only after the optimum conditions for the sensitive cyclization and ketone reduction steps had been found.

The structure **41b** was assigned to the Stobbe product on the basis of the n.m.r. spectrum which shows a singlet for an acid proton at τ 0.04, insignificant absorption in the vinyl proton region and the characteristic quartet and triplet pattern of the ethyl group at 5.9 and 9.0 respectively. It is likely that the half-ester is actually a mixture of geometrical isomers. On methylation with diazomethane, the methyl ethyl ester **41c** was obtained. The n.m.r. spectrum of the diester **41c** differs from that of the half-ester **41b** by the absence of the acid proton peak at τ 0.04 and the appearance of a new three-proton singlet at 6.35 attributed to the ester methyl group. The diester **41c** has no absorption in the vinyl proton region, again confirming the correctness of the assignment of the double bond in the half-ester **41b** to the *exo* position. The *endo* isomer would have a vinyl proton. It has the expected parent ion (342.1832) in the mass spectrum and losses of 31 (CH_3O) and 45 (C_2H_5O) confirms the presence of the methyl

and ethyl ester functions. Hydrolysis of the half-ester **41b** gave the diacid **41a** which exhibits the appropriate (300.1369) parent ion peak in the mass spectrum. Sublimation of the diacid gave the anhydride **50** which, like the half-ester and diester, shows no vinyl proton absorption in the n.m.r. spectrum. The anhydride **50** has the expected parent ion peak, (283.1249) in the mass spectrum and characteristic infrared (i.r.) absorption (1845, 1775, 1232 cm^{-1}) for the anhydride function. It has an ultraviolet (u.v.) absorption maximum at 307 nm, indicative of the C_6H_3-C=C-CO_2 conjugated system and supporting the *exo* assignment of the double bond. Formation of only the *exo* olefinic half-ester in the Stobbe reaction of the tricyclic ketone **14** may be contrasted with the predominant formation of the *endo* olefinic half-ester when benzsuberone was the substrate. The implication is that in a seven-membered ring with a fused benzo substituent there is a steric preference for an *endo* rather than an *exo* double bond.

The isolation of the acids **43a** and **44a** from the hydrolysis-decarboxylation of the half-ester **41b** rather than the expected olefinic acid **51a** suggests that disproportionation had taken place. There is a considerable gain in resonance energy as a result of the disproportionation reaction. In the hydrolysis-decarboxylation of the Stobbe product from benzsuberone no disproportionation was observed

because the seven-membered ring cannot be aromatized. From the hydrolysis-decarboxylation followed by hydrogen fluoride-catalyzed ring closure of the Stobbe product from 1-tetralone Johnson *et al*[70] obtained 2,3,3*a*,4,5,6-hexahydro-1*H*-phenalen-1-one in addition to the expected tetrahydrophenalenone. They recognised the hexahydrophenalenone as being a disproportionation product, although they were not able to isolate the dehydrogenated counterpart. They were also unable to determine whether the acid disproportionated before ring closure, or whether the tetrahydrophenalenone itself disproportionated. However, the acid was known to disproportionate on distillation.

The presence of the δ lactone ring in **42**, whose molecular formula follows from the mass of the parent ion (256.1411), is supported by the i.r. absorption at 1775 cm^{-1}. The presence of the benzene ring in the acid **43a** and its ester **43b**, and of the naphthalene ring in acid **44a** and its ester **44b** were established by n.m.r. spectra and confirmed by mass spectra. The acid **43a** shows an aromatic three-proton singlet at τ 3.23. Although the three aromatic protons in **43a** have different chemical environments, they may be expected to have very similar chemical shifts. The parent ion in the mass spectrum of **43a** has the appropriate precise mass (258.1615) and the expected mass of the parent ion of the ester **43b** is also observed. Moreover, in the

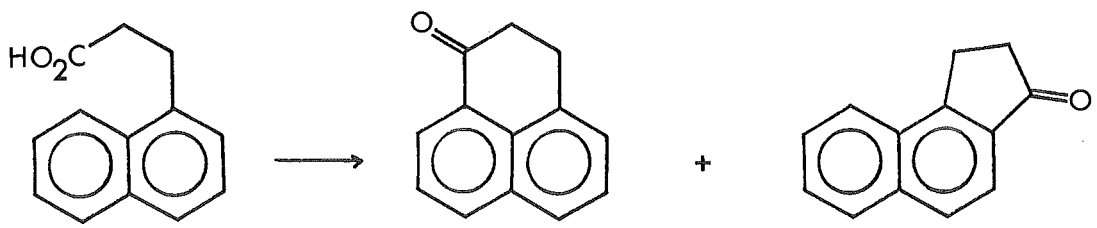
spectrum of each compound the base peak is formed by cleavage of the propionic acid side chain (loss of 73) and the methyl propionate side chain (loss of 87), respectively. Such cleavage gives rise to the same, resonance-stabilized, benzyl-type cation. The n.m.r. spectrum of ester **44b** exhibits absorption by the α-naphthyl-type proton at 2.29 and by the two β-naphthyl-type protons in the same ring at 2.93. These three protons are coupled and a multiplicity of lines is observed. The two β-naphthyl-type protons in the second aromatic ring have non-identical environments but their chemical shifts are the same and these protons absorb as a singlet at 3.03. The rest of the spectrum shows the absorption of the three methoxyl protons at 6.50, the six benzylic protons centred on 6.9, the two protons adjacent to the methoxy carbonyl function at 7.4 and the four alicyclic methylene protons at 8.1. Each of the parent ions in the mass spectrum of **44a** and **44b** has the requisite precise mass. Furthermore, cleavage of the propionic acid (ester) side chain is no longer the most important fragmentation, since this would have cleaved a bond to an aromatic ring. Instead the ester **44b** shows preferred loss of 73 corresponding to the $CH_2CO_2CH_3$ fragment, since this loss now generates a benzyl-type cation. Similarly the acid **44a** shows preferred loss of 59 (CH_2CO_2H) to give the same cation.

When the lactone **42** was reduced with red phosphorus and iodine in acetic acid, besides the expected acid **43a** the fully aromatized acid **44a** was also obtained. This is further evidence that lactones of the structural-type of **42** undergo acid-catalyzed isomerisation to their corresponding olefinic acids. In this case the olefinic acid may then reform the lactone or disproportionate to the acids **43a** and **44a**.

The structure of the hydrocarbon 3-ethyl-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**52**) which was obtained from the aromatization of the acid **43a** and to a lesser extent from that of the ester **43b**, was established by n.m.r. It shows the single α-naphthyl-type proton as a quartet at τ 2.28 and the two β-naphthyl-type protons in the same ring as a multiplet at 2.87. The two β-naphthyl-type protons in the second ring resonate as a singlet at 2.98. (The aromatic part of the spectrum is closely similar to that of ester **44b**.) The four benzylic-type protons in the seven-membered ring display broad absorption at 6.8 overlaid by the quartet pattern of the benzylic-type methylene of the ethyl group at 7.0. The four protons of the alicyclic ethylene group display a characteristic broad "quintet" at 8.0 and the protons of the methyl group exhibit a triplet of 8.69. In the mass spectrum the parent ion has the required precise mass (210.1405) and the most important

fragmentation—that of the methyl group to form the same benzyl-type cation as formed from **44a** and **44b**—support the assigned structure.

When the ester **44b** was cyclized using anhydrous hydrogen fluoride, only the product from *peri* closure was detected. When Fieser and Gates[43] cyclized 3-(1'-naphthalenyl)propionic acid[92] under similar conditions 6% of the product resulted from *ortho* closure.



89 81% 6%

That the cycloheptanaphthalenyl propanoate **44b** did not undergo *ortho* closure reflects the activation of the *peri* (4') position relative to the *ortho* (2') position by the four-carbon bridge fused across the opposite *peri* positions. The naphthalenyl propionic acid **89** does not have this activation, and the competitive *ortho* closure can thereby occur. The ketone **45** which resulted from the closure of the ester **44b**, displays a two-proton AB quartet with centres at 2.08 τ and 2.79 τ (J = 7.5 Hz) arising from the aromatic proton adjacent to the carbonyl group and the

adjacent aromatic proton in the same ring, respectively. The two aromatic (β-naphthyl-type) protons in the second ring resonate at 2.92 τ.

The compound obtained from prolonged cyclization reactions of the ester **44b** or from the treatment of the ketone **45** with DDQ was characterised as the enone **53**. The longest wavelength λ_{max} of **53** occurs at 415 nm and the compound is yellow, reflecting the extended conjugation. This extended conjugation is also reflected in the very low frequency of the carbonyl absorption (1635 cm^{-1}) and in the n.m.r. absorption of the vinyl protons which appear at low τ, overlapping the aromatic region. The spectrum of the aromatic and vinyl protons exhibit eleven lines which are composed of four AB quartets with one line from each of two of the quartets being superimposed at 450 Hz. The doublet at lowest field (1.58, J = 7 Hz) is clearly the aromatic proton adjacent to the carbonyl group. Irradiation at 505 Hz caused the disappearance of the peak at 443 Hz and a reduction in the intensity of the (combined) 450 Hz peak and an increase in the intensity of the 446 Hz peak. Thus, the 443 and part of the 450 Hz peak represents the second component of the AB quartet (2.55, J = 7 Hz) and is assigned to the aromatic proton in a *meta*-type relationship to the carbonyl group. The doublet in this region at highest field (3.41) was assigned to the vinylic proton α to the

carbonyl group. The same splitting (10 Hz) is exhibited by the peaks at 460 and 450 Hz. This latter doublet (2.42) was accordingly assigned to the second vinylic proton, that which is adjacent to the aromatic ring. Good analogy for these assignments is provided by the spectrum of, e.g., benzylidene acetone. Finally there remains the quartet at 453, 446, 438 and 431 Hz. This was attributed to the two remaining aromatic protons with the one adjacent to the seven-membered ring being assigned the higher-field absorption (2.74) and the one adjacent to the vinylene function assigned the lower-field absorption (2.52).

The Clemmensen reduction of the ketone **45** gave excellent yields (>90%) of the hydrocarbon **46** when the reaction was conducted for a short time, but only moderate yields when longer reflux periods were used (50% after 24 hours reflux). From the reaction of longer duration a considerable amount of yellow, high melting dimers (M^{+} = 440, 442) was obtained. Dimers were also obtained from the aprotic catalytic reduction of **45**, but not from the treatment of the hydrocarbon **46** with mineral acid when the main products were the ketone **45** and enone **53**. The dimerisation of **46** is therefore solely the result of a reductive process. The Clemmensen reduction of 1-oxo-1*H*-phenalene was reported to be unsuccessful. A short duration reaction was carried out on this enone to see if

its failure to form the required 2,3-dihydro-1*H*-phenalene was the result of a competitive or subsequent reaction to produce dimer. Dimerisation did occur, but at a rate much faster than that observed in the reaction of the cyclohepta-oxophenalene **45**, such that even after a short reflux period the major product was dimer, despite not all the starting material having reacted. The slower rate for the dimerisation of **45** is probably a reflection of its greater bulk. The hydrocarbon **46** has infrared, ultraviolet, n.m.r., and mass spectra analogous to those of dipleiadane, with appropriate allowance for the one less methylene group.

The compounds encountered in the alternative and less efficient route to **46**, the ketone **47** and the hydrocarbon **48**, show spectral characteristics similar to those of their homologues (**30** and **31**) which were intermediates in the synthesis of dipleiadane. The hydrocarbon **49**, the main product from this synthesis, with which the hydrocarbon **46** was formed concurrently, was differentiated from **46** by its n.m.r. and ultraviolet spectra. The n.m.r. spectra of **49** displays resonance by five aromatic protons as a multiplet centred at 2.83 τ (cf a four-proton singlet at 3.09 τ for **46**), and broad resonances for the five benzylic-type protons at 7.0 τ (cf eight at 7.0 τ) and for eight alicyclic protons at 8.15 τ (cf six at 8.1 τ). The ultraviolet spectrum of **49** shows an ε_{max} at 292 nm for the B-band, compared with 298 nm shown by **46**. The B-band is indicative

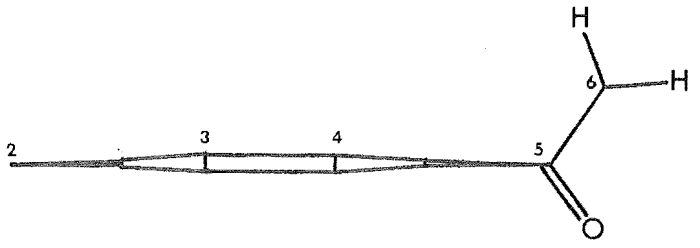
of the substitution pattern of the naphthalene nucleus, and the decrease in the wavelength at ε_{max} for **49** cf **46** is comparable to the decreases shown in methylnaphthalenes when substitution is β rather than α or, when, in polymethylnaphthalenes the number of substituents is decreased. It is surprising that when the hydrocarbon **48** dehydrogenates that the *cd* isomer is preferentially formed, in that dehydrogenation towards this isomer is activated only at one site (C-3a), whereas dehydrogenation towards the *fg* isomer is activated at two sites (C-3a and C-5a). Obviously the *cd* isomer is preferred on the grounds of steric strain energy. The substitution pattern in the *cd* isomer is *peri* and *ortho* and this can more readily accommodate the six- and seven-membered alicyclic rings than the di*peri* pattern in the *fg* isomer.

The Synthesis of 5,6,7,8-Tetrahydrocyclohepta[*fg*]acenaphthene (**57**)

Fieser has characterised most of the compounds encountered in this synthesis by their percentage elemental composition, their chemical properties, and their melting points. When we repeated the synthesis we characterised the compounds spectrally and our assignments were confirmed by comparing our melting points with those of Fieser.

The aromatic protons in the n.m.r. spectrum of the ester **55b** give well-defined resonances, and these were assigned by decoupling experiments. The n.m.r. spectrum of the diketone is remarkably simple. The aromatic proton resonances at 2.52 and 2.64 τ and the singlet at 6.57 τ are broadened relative to the other (downfield) aromatic proton resonances and the singlet at 6.95 τ. Irradiation at 6.57 τ caused the resonances at 2.52 and 2.64 τ to be sharpened so that their heights and half-height widths were comparable to those of the other peaks in the aromatic region. This is indicative of a small coupling which could be expected between the protons of the *ace* bridge, as the dihedral angle between the planes containing these protons and the carbons to which they are bonded is close to 90°, which is the angle which best favours coupling along four bonds[124]. Hence the singlet at 6.57 τ is attributed to the protons of the *ace* bridge, despite the corresponding protons in the hydrocarbon

57 resonating at 6.77 τ. The downfield shift of these protons is the result of the electron-withdrawing groups substituted *para* to the methylene groups that they are part of. The singlet at 6.95 τ which we attribute to the protons of the bridge carbons α to the carbonyl functions suggests that the seven-membered ring is planar. If it were not planar the bridge protons of the seven-membered ring could be expected to have distinctly different chemical shifts as one of the protons would be orientated parallel with the carbonyl function, and hence deshielded, and the other away from it. A high rate of ring inversion could



account for these protons coalescing to a singlet, but a model of the molecule with this conformation shows the seven-membered ring to be very rigid, and it is improbable that any ring inversion would occur at all. The spectrum of **56** does not vary over a temperature range of -60 to +180°, except that at 180° the resonance at 6.57 τ is moved upfield to 6.72 τ. The infrared spectrum of the

diketone supports the assignment of a planar seven-membered ring. The $\nu_{C=O}$ at 1660 cm^{-1} is notably low for an aromatic carbonyl function (usually 1700-1680 cm^{-1}) and this suggests that the aromatic nucleus and carbonyl function are coplanar in order to achieve maximum conjugation. (Pleiadenones have $\nu_{C=O}$ = 1655 cm^{-1} [12], but in these cases the carbonyl function is conjugated with two aromatic nuclei.)

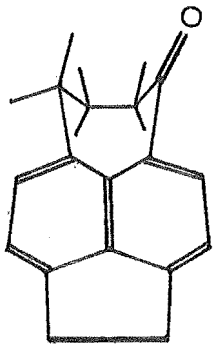
The closure of the oxo ester **55b** to form the diketone **56** is a unique reaction. As was discussed earlier (page 173), the reaction appears to be unfavoured on stereochemical and electrostatic repulsion grounds. The reaction proceeds only when vigorous conditions which produce a strongly electrophilic centre are used. The electrophilic attack by the aluminium chloride-carbethoxy complex on the aromatic nucleus forms a Wheland intermediate which is thought to relieve the steric strain inherent in the acenaphthene molecule[45]. Acenaphthene is further more favoured than naphthalene because the 5- and 6-(*peri*)carbons of acenaphthene are further apart than their counterparts in naphthalene and can therefore accommodate the seven-membered ring more readily.

The n.m.r. spectrum of the cycloheptaacenaphthene **57** exhibits the familiar quintet at 8.0 τ for the dimethylene bridge of the seven-membered ring. The benzylic-type protons

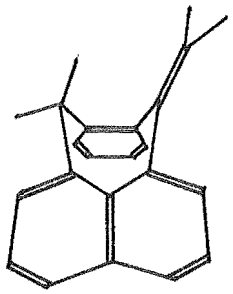
show their stereochemical difference. The protons of the seven-membered ring resonate as a broad peak at 6.9 τ (cf for dipleiadane) while the protons of the five-membered ring give rise to a singlet at 6.77 τ (cf 6.68 for acenaphthene). During the formation of the cycloheptaacenaphthene **57** a small amount of the octahydrocycloheptaacenaphthene **59** resulted from the former being further reduced. The reduction of a naphthalene nucleus under such mild conditions is unusual, and is probably a further reflection of the strain in the acenaphthene structure. The compound **59** has spectral characteristics similar to those of its homologous cycloheptaphenalene **47** , allowing for the difference of one methylene. Its elemental analysis and mass spectrum ($M^{\dagger}$ = 212) are consistent with the formula $C_{16}H_{16}$. Its n.m.r. spectrum has the required integral ratio for resonances in the expected regions.

When the hydrogenation of the diketone **56** was incomplete the mono ketone **58** was isolated. It was identified by its infrared ($\nu_{C=O}$ = 1655 cm^{-1}), mass ($M^{\dagger}$ = 222), and n.m.r. spectra. The n.m.r. spectrum shows the quartet and singlet pattern in the aromatic proton region which has previously been observed for *peri* naphthalenes with one α substituted carbonyl function. The singlet of the *ace* bridge protons appears at 6.7 τ and at 6.93 τ there is a triplet which we attribute to the

benzylic-type protons of C-8 which are coupling with the C-7 protons. Also coupling with the C-7 protons are the C-6 protons which appear as a triplet at 7.17 τ. The C-7 protons themselves appear as fine structure centred on 7.72 τ. The coupling constants for the C-6 and C-8 protons suggest that either the seven-membered ring is planar or it is of a boat-type conformation in which inversion is taking place that rapidly that the protons are being observed only as one time-averaged resonance. If the molecule existed in a boat-type conformation it could be expected to have ring inversion properties similar to its stereochemical analogue 7-methylene-7,12-dihydropleiadene (**90**). The hinge (C-12)



58



90

protons of the methylene pleiadene coalesce at +40°[12]. The free energy of inversion for **58** could be expected to be of the same order as that for **90**, probably being lowered by the greater flexibility about the bridge (C-6, C-7)

carbons, but on the other hand increased by the longer C-6, C-7 bond and decrease in the angles of the seven-membered ring. A comparison of models **58** and **90** suggests that **58** is less likely to invert. However, the spectrum of **58** did not change even when observed at -60°. That there was no increase in the number of resonances in the spectrum suggests that the seven-membered ring of **58** is planar. This assignment is reinforced by the exceptionally low C=O frequency which suggests that the carbonyl function and aromatic nucleus are coplanar.

A Comparison of Spectral Properties of the *peri*-Naphthalenes

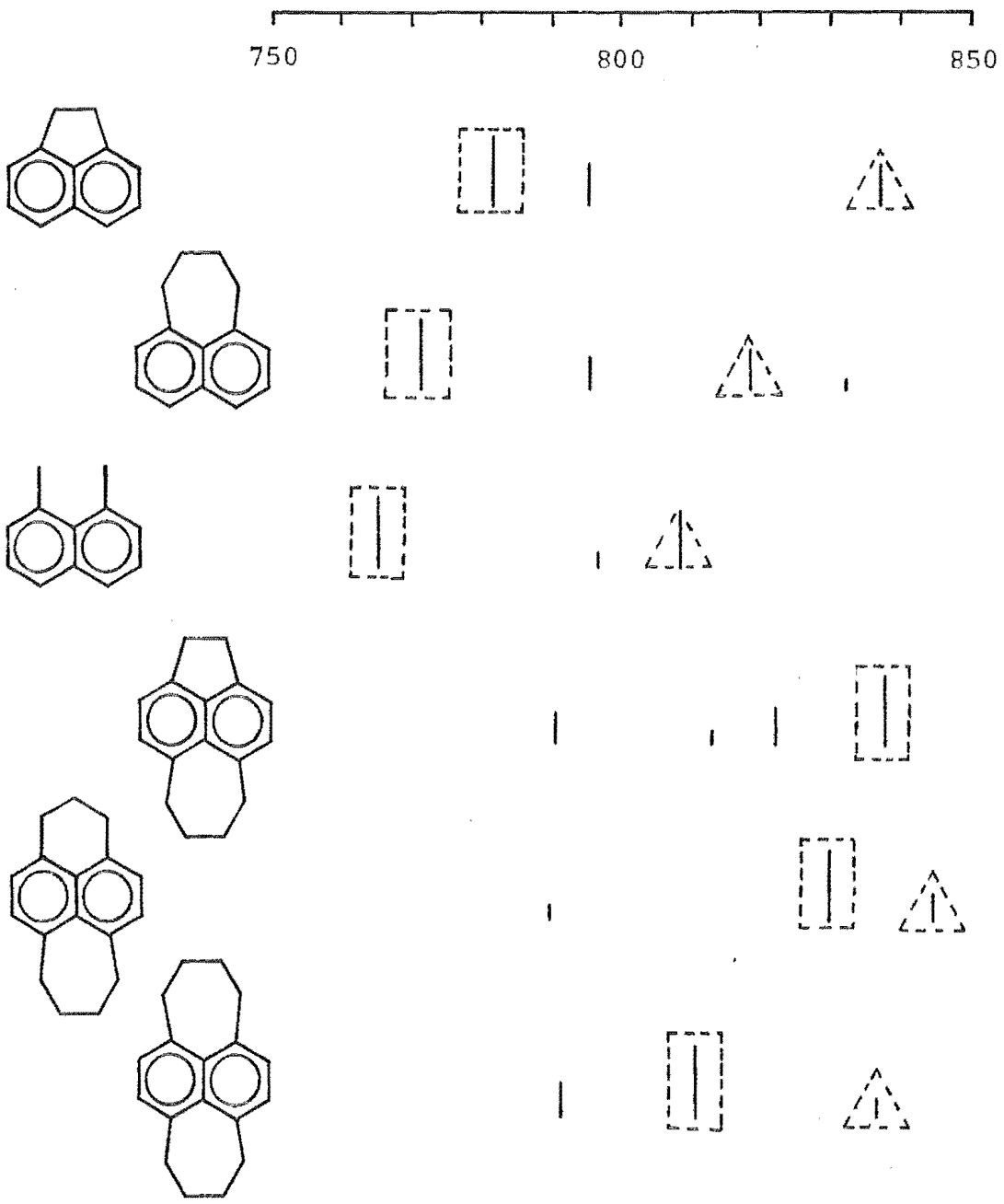
In the infrared spectrum of 1,8-substituted naphthalenes the region of interest is that of 700-900 cm^{-1} in which the out-of-plane bending vibrations of the aromatic carbon-hydrogen bonds occur. These vibrations can be imagined as resulting from the oscillation of the aromatic carbons as a rigid structure through the plane of the aromatic hydrogen atoms[125]. Topsom *et al*[32] observed that 1,8-disubstituted naphthalenes give two bands in this region. Only one band would be expected owing to the symmetry of the molecule which results in two sets of three adjacent hydrogens. (Earlier workers showed that the out-of-plane bending vibrations for the hydrogen atoms attached to a benzene nucleus are characteristic for the number of adjacent

hydrogen atoms, and hence for the substitution pattern of the ring. These observations were extended to naphthalenes where the two rings may be considered as two benzene rings, both *ortho* disubstituted. It was further shown that where a substitution pattern occurs that gives rise to a combination of different adjacent hydrogen relationships (e.g. 2,5-disubstituted naphthalene) the bands of both sets of hydrogens occur, each being independent of the other[33].) Topsom *et al* further observed that for 1,8,x trisubstituted naphthalenes three bands rather than the expected two occur, with the exceptions of 1,3,8-isomers, which tend to give rise to only two bands. They suggest that the differing behaviour of the latter (the absence of the additional unexpected band) may be the result of their lesser symmetry, or conversely, the extra band observed for 1,8 substituted naphthalenes results from their symmetry.

The aromatic C-H bending bands for the *peri* naphthalenes encountered in this work are shown in table I. The values of these bands found in 1,8-dimethylnaphthalene[32] are included for comparison. The 1,4,5,8-tetrasubstituted hydrocarbons all show bands in the region 800-840 cm^{-1} which has been assigned as the region characteristic for the two adjacent hydrogen bands[126]. The more intense band in this region for each of the hydrocarbons has been assigned to the C-H bending mode of the adjacent hydrogens.

TABLE I

Infrared characteristics of the *peri* cyclic naphthalenes



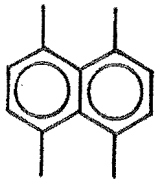
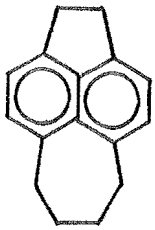
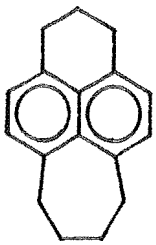
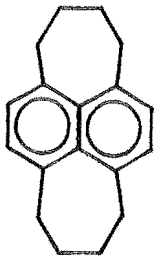
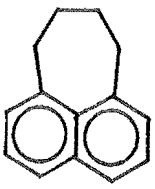
These are shown in squares and show an increase in frequency from dipleiadane to acepleiadane. This may be a reflection on the increasing rigidity of these molecules, and thus the increasing energy of the bending vibrations. This is the same trend observed for the 1,8-disubstituted naphthalenes in going from 1,8-dimethylnaphthalene to acenaphthene where the most intense band is in the region 740-780 which has been ascribed to the C-H bending mode of three adjacent hydrogens. Topsom *et al* imply the assignment of the lower and less intense band of acenaphthene at 743 cm^{-1} to this vibrational mode, but we suggest that this assignment is erroneous, and the more intense band at 782 cm^{-1} is from this vibration. Note that for the 1,8-disubstituted naphthalenes and 1,4,5,8-tetrasubstituted naphthalenes there appears to be a characteristic band of weak to medium intensity at c.a. 795 and 790 cm^{-1} respectively. The extra band observed in 1,8-substituted naphthalenes could possibly result from an asymmetric bending mode which is enhanced in 1,8-substituted owing to the distortion in the molecule arising from *peri* interaction. The bands which may be the result of this type of vibration are enclosed in a triangle. The disappearance or decrease in intensity of the extra band in 1,3,8-trisubstituted naphthalenes may be the result of the substituent modifying the molecule (e.g. 3-bromo-1,8-dimethylnaphthalene on page 5) such that vibrations of this

type are less favoured.

The ultraviolet characteristics of the dicyclo *peri* naphthalenes are listed in table II. 1,4,5,8-Tetramethylnaphthalene[28] has been included for comparison. The ultraviolet spectra of these hydrocarbons not only show absorption at characteristic wavelengths but they also have a characteristic shape. Like naphthalene itself the dicyclonaphthalenes give rise to three bands. The band at lower wavelength is intense (1880-2150 m^2 mol^{-1}) and is a single peak with maximum absorbance at 236-238.5 nm. The middle band is broad with fine structure and inflections and rises to a maximum intensity (850-970 m^2 mol^{-1}) at 298-299.5 nm. The band of higher wavelength is a single peak at 331-2 nm of low intensity (260-460 m^2 mol^{-1}). The middle (299 nm) and lower (236 nm) bands show a decrease in intensity from dipleiadane to acepleiadane, while the higher (331 nm) band shows an increase. There is also an increase in fine structure in the middle band in going from dipleiadane to acepleiadane. The latter two trends (i.e. the increase in intensity of the higher band and increase in fine structure of the lower band) have been observed for the series perinaphthane, 1,8-dimethylnaphthalene, and acenaphthene, and it has been suggested that they result from strain[127]. This is a reasonable suggestion because the higher band results from a transition which reflects

TABLE II

The ultraviolet characteristics of the *peri* cyclic naphthalenes

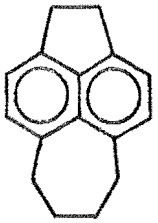
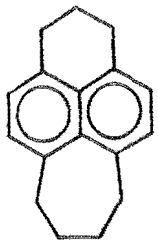
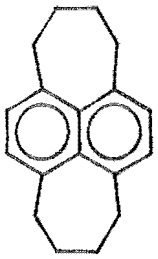
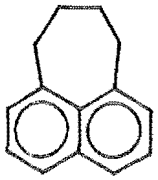
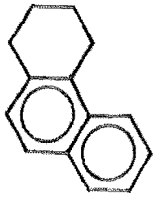
	233	290	296	307	318	326	334
	236	289	298.5	310.5	316.5	324.5	331
	236	288	298	309	316	325	331
	238.5	289	299.5	311	317.5		332
	232	278	288	299	308	318	323

the longitudinal (e.g. in naphthalene the direction $\overleftarrow{27}$ across the two aromatic rings) polarization of the molecule. It is feasible that in-plane distortion will increase this polarization, and this is reflected in the intensities of the higher band from dipleiadane to acepleiadane, for in-plane distortion will also increase in this order. The position of the middle band reflects the degree of (hyper)conjugation of α substituents in the naphthalene nucleus because this band results from a transition of transverse (e.g. in naphthalene the direction $\overleftarrow{14}$) polarization and an increase in polarization up and down the rings results in a bathochromic shift. Hence λ_{max} for this band in dipleiadane is 11.5 nm higher than that in pleiadane, or 13.5 nm higher than that found for naphthalene.

The positions of nuclear magnetic resonances of the pericyclic hydrocarbons are listed in table III. All samples were dissolved in carbon tetrachloride. The dicyclo compounds all show a singlet for the aromatic protons in the region 3.07-3.13 τ, a broad resonance of the benzylic-type protons at 6.90 τ, and a multiplet which approximates to a quintet of a characteristic shape at 8.0-8.06 τ. The multiplet arises from the protons of the bridge (C-2 and C-3 in dipleiadane) and is also observed (at 8.15 τ) for the bridge protons of 1,2,3,4-tetrahydroxyphenanthrene. Acepleiadane also has a sharp

TABLE III

The n.m.r. characteristics of the *peri* cyclic naphthalenes

	Ar-*H*	Ar-C*H*$_2$		Alicyclic C*H*$_2$	
	3.07(4)	6.77(4)	6.90(4)	8.0(4)	
	3.09(4)	6.90(4)	7.05(4)	8.06(4)	8.06(2)
	3.13(4)	6.90(8)		8.06(8)	
	2.2-3.3(6)	6.86(4)		8.02(4)	
	2.0-3.1(6)		7.07(4)		8.15(4)

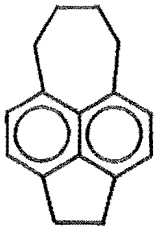
resonance at 6.77 τ resulting from the four protons of the *ace* bridge. Peripleiadane has resonances centred on 7.0 and 8.06 τ arising from the six-membered *peri* cycle which superimpose those of the seven-membered ring.

From an E.P.R. study of dipleiadane Claridge[134] has suggested that the rate of inversion is comparable to the hyperfine frequency at +55°, which was calculated to be 3.5×10^8 per second. Temperature-variable n.m.r. studies reinforce this suggestion of a high rate of ring inversion as little change was discernible in the spectrum over a temperature range of -60 to +180°.

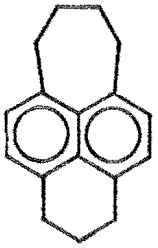
The predominant fragmentation ions observed in the mass spectra of the pericyclic hydrocarbons are listed in table IV. These exhibit a pattern corresponding to the loss of CH_3, C_2H_4, C_2H_5, and C_3H_5 fragments. C_3H_7 and C_4H_9 losses are also observed but these do not have corresponding metastable peaks (and it is noteworthy that the C_4H_9 loss does not occur in the mono pericyclic pleiadane). The ion *m/e* = 165 shows an enhanced relative intensity in the spectra of the dicyclo compounds, and this is probably due to the formation of the mesomerically stabilised phenalenyl cation. The intensity of the *m/e* = 207 (M^+ -1) ion of acepleiadane may be a further reflection of the strain in this molecule. Cleavage of a hydrogen radical from an α carbon of the seven-membered ring would result in

TABLE IV

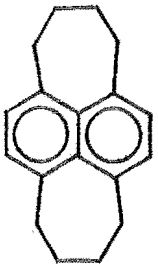
The predominant fragmentations in the mass spectra of the *peri* cyclic naphthalenes



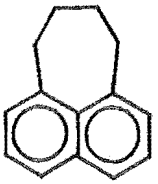
57



46



17

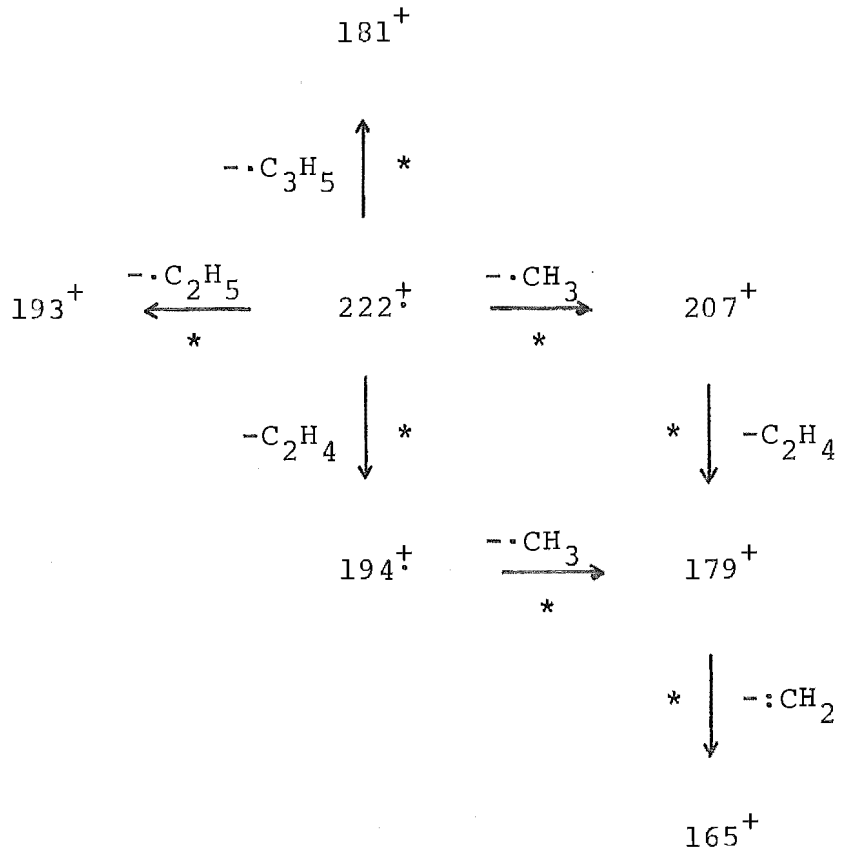


5

$M^{+\cdot}$	208(100)	222(100)	236(100)	182(100)
	207(66)	208(6)		
-15*	193(53)	207(32)	221(8)	167(81)
				165(46)
-28*	180(62)	194(29)	208(4)	154(24)
-29*	179(46)	193(15)	207(5)	153(40)
				152(41)
-41*	167(36)	181(12)	195(4)	141(24)
-43	165(61)	179(25)	193(5)	139(8)
-57	151(11)	165(25)	179(9)	124(<1)

a positive charge on the carbon to which the five-membered ring is fused, thus allowing for a decrease in strain in the five-membered ring.

The fragmentation of peripleiadane is shown below as an example of the type of fragmentations exhibited by dicyclo *peri* naphthalenes. No precise mechanisms can be given for



the cleavages of hydrocarbon fragments, because these are known to be complex[114]. For the formation of the ion *m/e* = 179 the metastable of the loss from *m/e* = 194 is considerably more intense than that from *m/e* = 207.

The Nitro-acetoxylation of Carbocyclic Aromatics

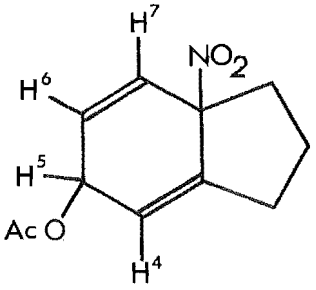
The diene products from the nitro-acetoxylation of carbocyclic aromatics were easily detected by infrared spectroscopy owing to their characteristic ester C=O frequency (c.a. 1740 cm^{-1}) and aliphatic C-NO_2 frequency (c.a. 1550). The aromatic acetoxy and nitro compounds had corresponding frequencies at c.a. 1765 and 1525 cm^{-1}. The n.m.r. characteristics were also appreciably dissimilar to those of the aromatic compounds formed concurrently during the reaction. The vinylic and allylic protons resonate between 3.5 and 4.5 τ, as opposed to 3.3 τ and lower for aromatic protons. From the results of previous work[60] the isomers obtained from the simple (symmetrical) bicyclic aromatic compounds were assumed to be geometrical (*cis-trans*) isomers. Each geometrical isomer presumably consists of a racemic mixture of enantiomers since each has two asymmetric carbons.

The assignment of protons to resonances for the indan adduct **67** was made by considering the effect of the structural environment on the chemical shift of the protons and the results of decoupling experiments. The more stable adduct which was isolated in a pure crystalline form was assigned the *cis* configuration with respect to the nitro and acetoxy functions on the grounds of the coupling constants for the protons on carbons-4, -5 and -6. These and chemical

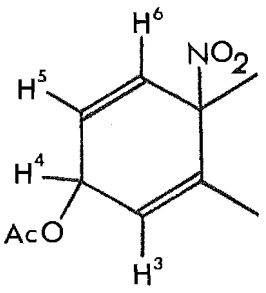
shift values for the stereoisomers of the indan adducts and the *o*-xylene adducts **91** are listed in table V. The five-membered ring of the indan adduct locks the six-membered dienic ring into a fixed boat conformation, such that it cannot flip from one boat conformation to the other. This dictates that the dihedral angle between the H^5-C^5-C^6 and H^6-C^6-C^5 planes and between the H^5-C^5-C^4 and the H^4-C^4-C^5 planes will be of the order of 25° for the *cis* isomer and 95° for the *trans* isomer. The Karplus equation[124] suggests coupling constants of 7 Hz and 0 respectively at these angles. Those observed are J_{45} = 5 Hz and J_{56} = 3.9 Hz for the stable isomer and J_{45} = 3 Hz and J_{56} = 2.5 Hz for the unstable isomer. These results confirm Blackstock's[58] assignments which were made on the basis of a comparison of the results obtained from competitive decompositions of the isomers and the assumed analogous decompositions of *cis*- and *trans*-1,5-dichloro-9,10-dihydro-9,10-anthradiols[128], and on the downfield shift of the H^4 and C^1H_3 resonances in the *trans* isomer with respect to the *cis*. This downfield shift was attributed to deshielding by the nitro and acetoxy groups, respectively. The deshielding of the allylic proton (H^5) in the *trans* isomer of the indan adduct relative to the *cis* isomer (a difference of 0.22 p.p.m.) is enhanced by comparison to that in the *o*-xylene adducts (a difference of 0.18 p.p.m.). This difference in deshielding and J_{45}

TABLE V

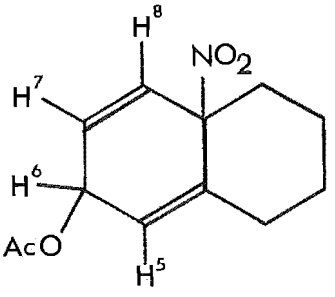
Chemical Shifts (τ) and J values for the nitro-acetoxy adducts of indan, *o*-xylene, and tetralin



67



91



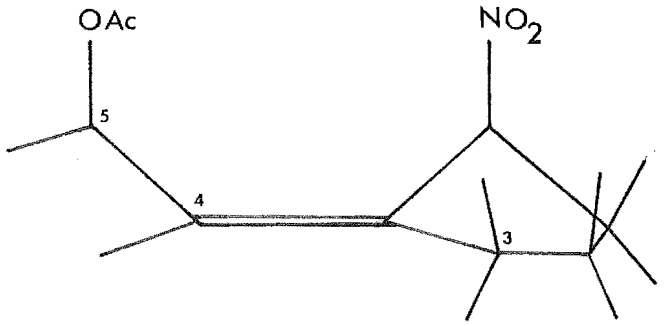
93

	cis	*trans* †		*cis*	*trans*		*trans*
H^4	4.0 τ	4.1	H^3	4.15	4.14	H^5	4.16
H^5	4.45	4.23	H^4	4.45	4.28	H^6	4.36
H^6	3.8	3.78	H^5	3.99	3.97	H^7	4.03
H^7	3.67	3.65	H^6	3.99	3.97	H^8	4.03
$OCOCH_3$	7.99	8.03		7.96	7.97		7.99
			C^1H_3	8.30	8.22		
			C^2H_3	8.22	8.17		
J_{45}	5.0 Hz	3.0	J_{34}	2.0	2.5	J_{56}	2
J_{46}	1.5	1.5	J_{35}	-	-	J_{57}	-
J_{56}	3.9	2.5	J_{45}	2.0	2.5	J_{67}	2
J_{67}	10.0	10.0	J_{56}	-	-*	J_{78}	-

† Estimated Values

* $\tau_5 = \tau_6$

and J_{56} constants for the *cis* and *trans* isomers, both in relation to each other and to their *o*-xylene counterparts, suggests that the conformation of the skeleton of the indan adduct is that of a rigid boat rather than planar, which is the preferred conformation for cyclohexa-1,4-dienes[129].



In contrast to the inequality of the J_5 constants for the *cis* and *trans* indan adducts, the adducts of *o*-xylene have constants of the same order. This, and their decrease in magnitude compared to the corresponding values for the indan adduct (or increase for the *trans* adduct), suggests that the more flexible *o*-xylene adducts either assume the preferred planar conformation, or that they are rapidly interconverting from one boat form to the other such that only a time-averaged n.m.r. spectrum is observed.

The diene region of the n.m.r. spectrum of **67** was computed* in the manner of Swalen and Reilly[132] using an

*The computations were kindly carried out by Dr. A.L. Wilkinson

NMRIT program[133]. The estimated chemical shifts and coupling constants are fed into the program which then gives possible transitions which may account for these lines. The more probable transitions are fed back into the program which then assigns them to a set of energy levels and by linear least squares refinement finds the best set of energy levels for these transitions. It then calculates coupling constants and chemical shifts required to give these refined energy levels and from these the intensities expected for the lines are calculated. The spectrum is then plotted and a comparison with the observed spectrum may then be made. The advantage of this program over others (e.g. LAOCOON) is that the energy levels are refined before the refinement of chemical shifts and coupling constants, and are thus constant during the latter refinement. In the LAOCOON program the energy levels vary during the refinement of chemical shifts and coupling constants resulting in the prolongment of the process whereby a computed spectrum is found to fit the observed one. As can be seen in figure 11 the computed values for coupling constants and chemical shifts are close to those assigned by empirical observation, and the computed and observed spectra are of comparable shape. The broadening in the 4.0 τ region of the observed spectrum is probably the result of H^4-H^3 coupling, which was not taken into account

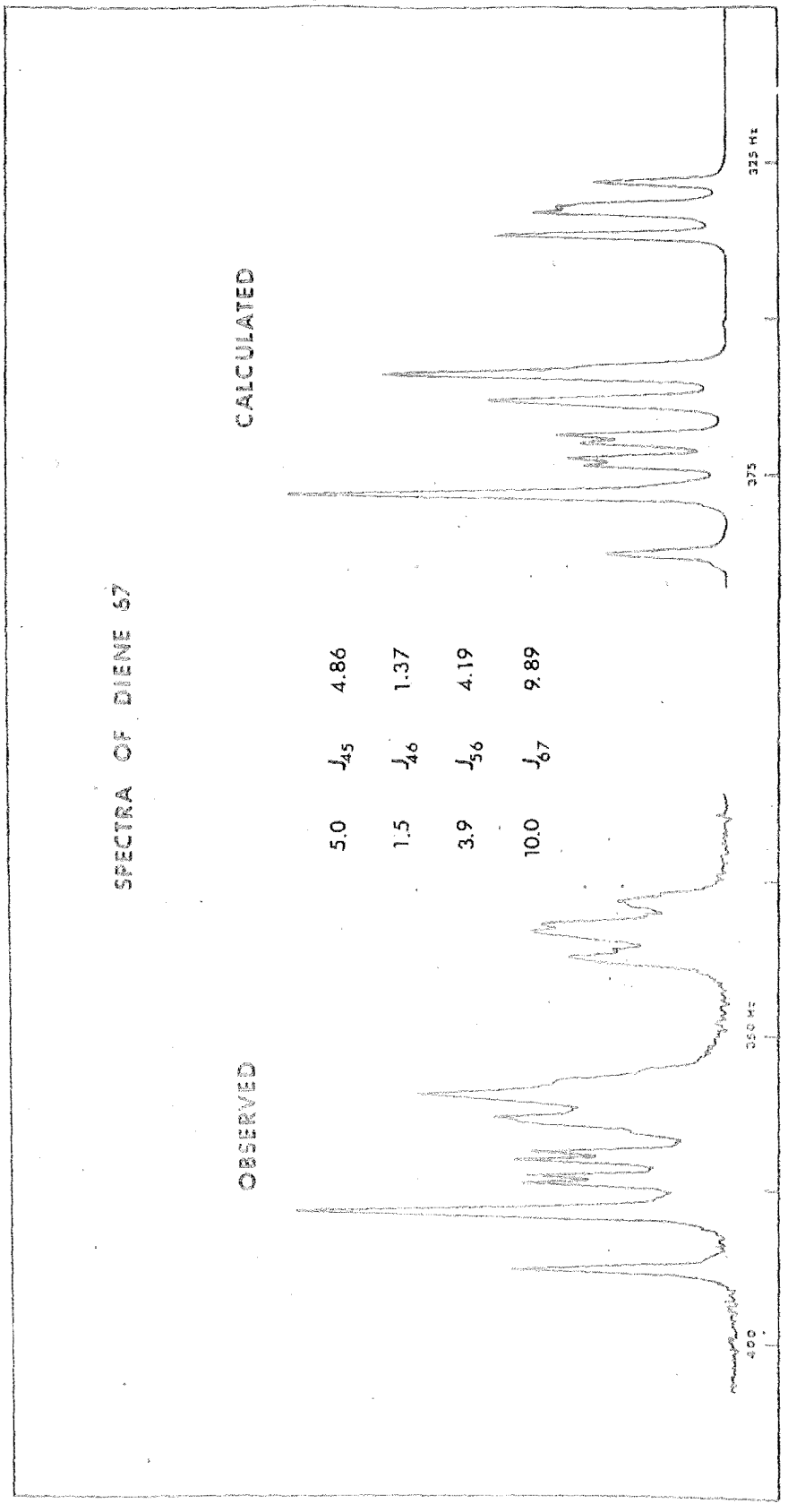
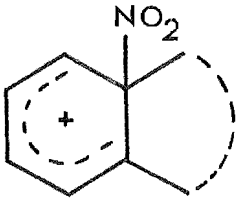

SPECTRA OF DIENE 67
OBSERVED
CALCULATED
5.0 J_{45} 4.86
1.5 J_{46} 1.37
3.9 J_{56} 4.19
10.0 J_{67} 9.89
400
350 Hz
375
325 Hz

FIGURE 11

when the computations were carried out. Coupling of a similar nature (C^2H_3-H^3) is observed in the adduct of *o*-xylene (**91**).

The *cis-trans* ratio for the indan adduct formation is as high as 80:20. The predominance of the *cis* isomer is in contrast to Blackstock's results with *o*-xylene and other methylbenzenes. This may be explained by a consideration of the stereochemistry of the Wheland intermediates which would be formed after electrophilic attack at a substituted carbon in the aromatic ring. For indan the intermediate is forced to retain its conformation with the C-NO_2 bond axial with respect to the six-membered ring. The acetic acid molecule displaced from the nitronium ion in forming the Wheland intermediate is therefore ideally located for addition to the *para* position leading to the *cis* adduct. In forming the more flexible Wheland intermediate for *o*-xylene the nitro group is not constrained to be axial and it is less probable that the displaced acetic acid molecule is as ideally located for the *para* addition. Competition by *trans* attack by a solvent acetic anhydride (or acid) molecule is then more pronounced. It is even possible that the *cis* adduct may be formed by a concerted cyclo-addition and it may be argued that the concerted addition is more probable in the case (indan) where the nitro group can only assume an axial orientation.

In the above discussion it has been presumed that at least *trans* adduct formation proceeds via a Wheland intermediate. This is suggested (further to the interpretations of Blackstock (page 36) by the high reactivity of indan relative to tetralin. This reactivity has been observed previously for electrophilic substitution[130] and is due to the transition state of indan being stabilised by the formation of a single bond between the carbons common to the two rings (C-3a and C-7a), owing to a release in strain energy in the five-membered ring; and to the transition state of tetralin being destabilised by the formation of a single bond common to both rings, because six-membered rings prefer to accommodate a double bond in an *endo* configuration rather than an *exo*[56]. In electrophilic attack at a substituted carbon of the aromatic ring of a carbocyclic benzene the above situation is complied with, for a Wheland intermediate of the structure **92** is formed.

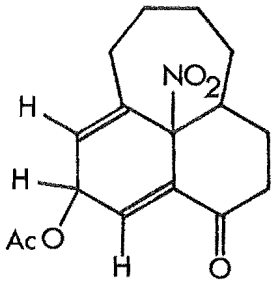


92

The n.m.r. of the stable tetralin adduct **93** (table V) was more simple than that of the indan adduct, and bore more similarities to *o*-xylene. Considering the somewhat greater flexibility of the tetralin diene this is not surprising: it is probable that the (time-averaged) spectrum is close to that of the planar conformation. On the basis of this work and Blackstock's results this more stable isomer was assigned the *cis* conformation. However, unlike Blackstock's result for *o*-xylene, but similar to indan adduct formation, the *cis* isomer was the major product (65:35). The same explanation for the predominance of *cis* product which was given above for indan can also be applied for tetralin. Although the Wheland intermediate of tetralin is more flexible than is the indan intermediate it is less flexible than that from *o*-xylene, and, in particular, the nitro group is forced to assume an axial or at least a semi-axial position with respect to the potential diene ring, but it cannot assume an equatorial position.

The dienes formed from 3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**), **68** and **69** , were assigned as the *trans* and *cis* diastereoisomers, respectively, of the structure shown. The observed ultraviolet wavelength (241 nm) for the enone chromophore was closer to the value calculated (using Woodward's rules[131]) for the structure **94** (242 nm) than that calculated for the structures **68** and **69**

(249 nm).



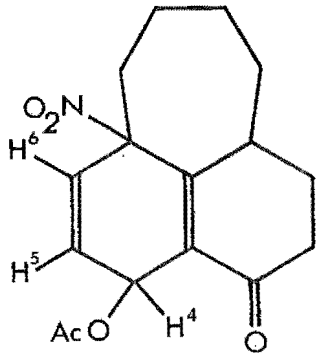
94

However, the differences are small, and the n.m.r. spectrum is clearly consistent with the structure **68** (or **69**) and not with **94**. Coupling constants as large as 10 Hz were observed (see table VI) and this is well in excess of the coupling constants (viz J_5) normally observed for structures of the type of **94** lacking vicinal vinyl protons (e.g., the corresponding constants for the adduct of hemimellitine **95** [60b] (table VI) and the J_5 values for adduct of indan **67** (table V)). A value of 10 Hz is, however, appropriate for the coupling constant of *cis* vinyl protons (which are present in **68** and **69**), and indeed Wilkinson[63] has observed a J value of 10.3 Hz for the splitting of the *cis* vinyl protons in the diene from 1,4 dimethylnaphthalene (XIX, page 39).

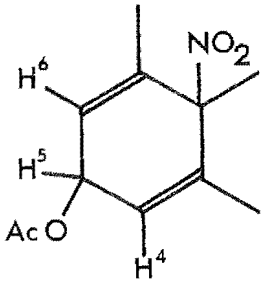
The compound **68** was assigned the *trans* configuration with respect to the nitro and acetoxy functions. Although the diene ring is flexible it is likely to favour

TABLE VI

Chemical shifts (τ) and *J* values for the nitro-acetoxy adducts of 3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**) and hemimellitine (**95**)



68 **69**



95

	trans	*cis*	*trans*	*cis*
H^4	3.73 τ	3.87		
H^5	3.63	3.80		
H^6	3.90	3.98		
J_{45}	4 Hz	3	4	2.5
J_{46}	0	0.75	-	-
J_{56}	9.5	10	4	2.5

the boat conformation which has the acetoxy function axial, as the other conformation brings the acetoxy function and carbonyl function into an eclipsed equatorial relationship which approximates the unfavoured 1,3 diaxial conformation. Conversely, the allylic proton (H^4) will be equatorial. The *cis* isomer is expected to have both nitro and acetoxy groups equatorial as the alternative conformation would place these groups in an unfavourable 1,4 diaxial ("flag-pole") relationship. The dihedral angle between the H^4-C^4-C^5 and H^5-C^5-C^4 planes therefore tends to 0° in the *trans* and 80° in the *cis* isomer. The Karplus equation thus predicts that the J_{45} value should be greater for the *trans* isomer **68** than for the *cis* isomer **69**, and this is what is observed. Furthermore, the dihedral angles between the H^4-C^4-C^5 and H^6-C^6-C^5 planes show the same tendencies (i.e. for the *trans* isomer the angle tends to 0°), and observations of coupling through four bonds[124] predict that H^4-H^6 coupling will be lesser for the angle which tends to 0°. The structure **68** shows no H^4-H^6 coupling but **69** has J_{46} = 0.75 Hz, thus supporting the above assignment.*

In both isomers the allylic proton (H^4) is shifted downfield (3.83 and 3.87 cf the usual 4.2-4.5 τ). This is probably the result of both the inductive and deshielding effects of the α substituted carbonyl function.

N.m.r. integral values suggest that the *cis* and *trans*

---

* H^4-H^7 coupling has also been observed for **69**, indicating further that **69** is the *cis* isomer.

isomers are formed in approximately equal proportions. It was predicted that deactivated aromatic nuclei would not undergo addition reactions of this type, owing to the destabilisation of the Wheland intermediate by the electron-withdrawing group. Yet for this compound 39% of the starting material reacted to form diene products, which compares favourably with the quantities of diene products formed from *o*-xylene (48%) and hemimellitine (44%). While the proposed Wheland intermediate would be deactivated by the electron-withdrawing carbonyl function the product diene is undoubtedly stabilised through conjugation of one of the olefinic bonds with the carbonyl function. This is shown by the low $\nu_{C=O}$ (1675 cm^{-1}) in the infrared.

In the diene products the nitro group is substituted at the 6a and not the 10b position. This supports the contention that the reaction is initiated by electrophilic attack by a nitronium (or incipient nitronium) ion as the 6a position is that position least deactivated by the carbonyl function towards electrophilic attack.

The diene region in the n.m.r. spectra of **68** and **69** were computed in the manner in which the spectrum of the indan adduct **67** was computed. The observed and calculated spectra of **68** are shown in figures 12 and 13 respectively. The calculated values for **69** are J_{45} = 3.57, J_{46} = -1.62, J_{56} = 9.89.

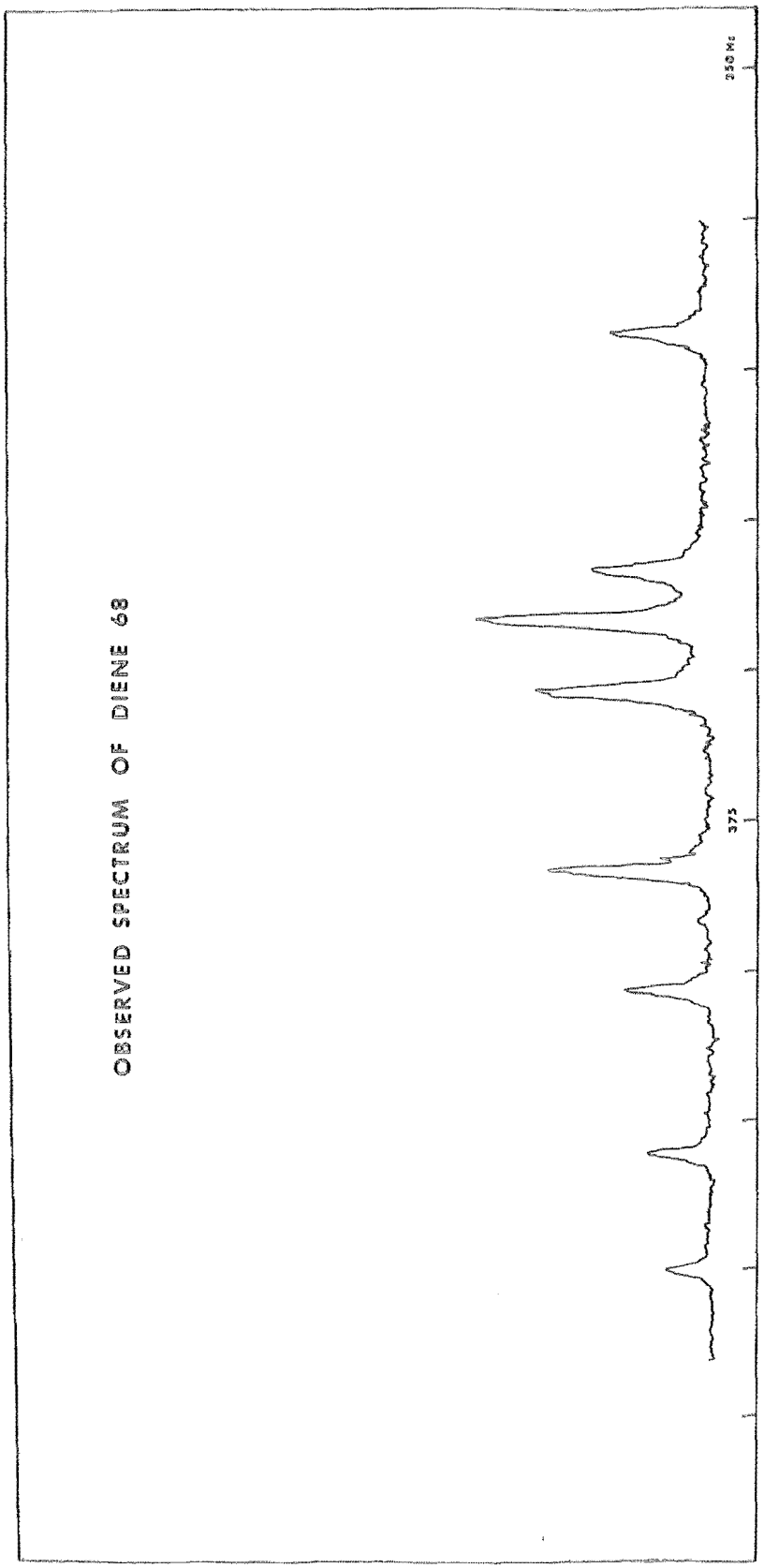


FIGURE 12

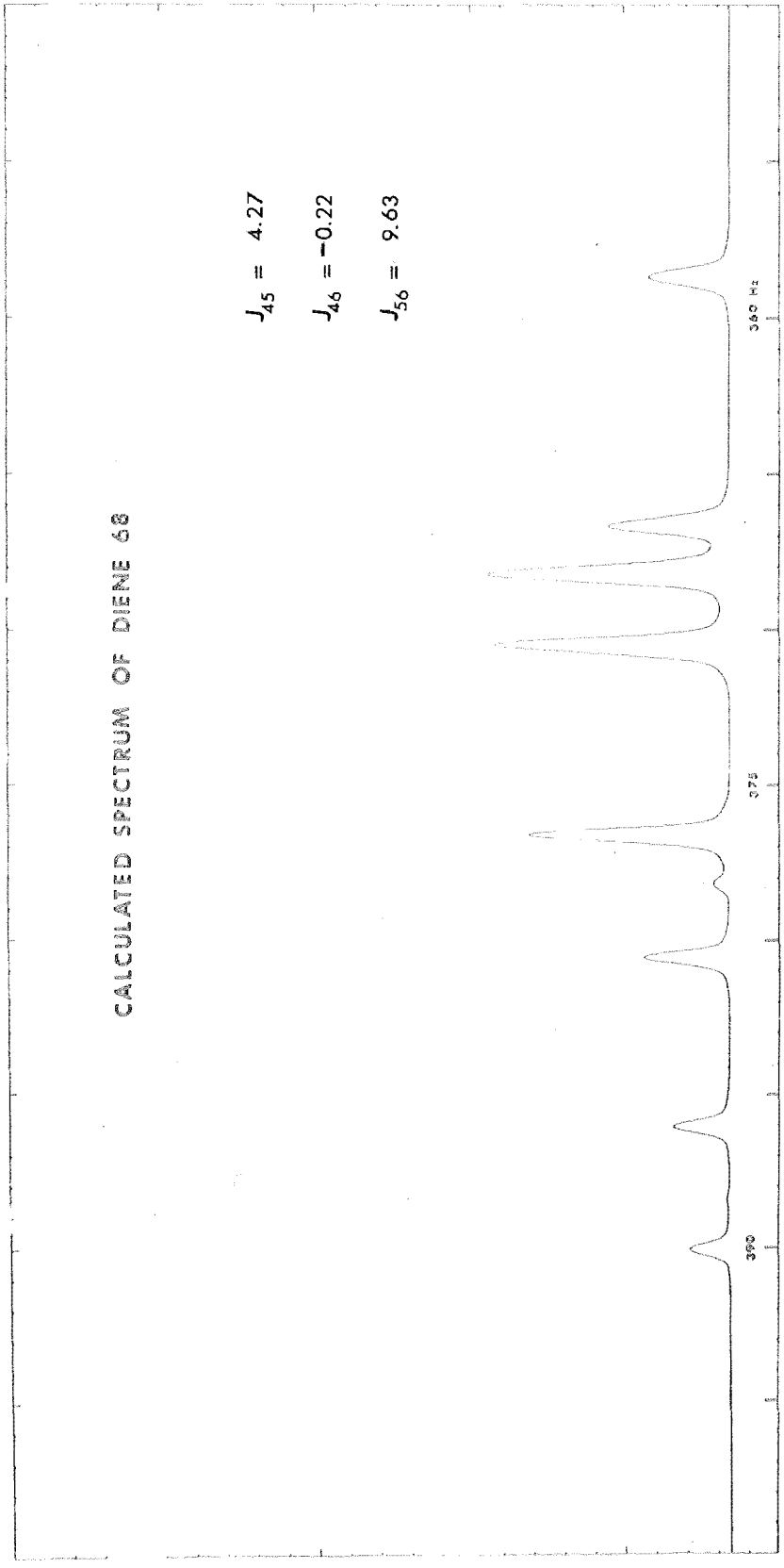
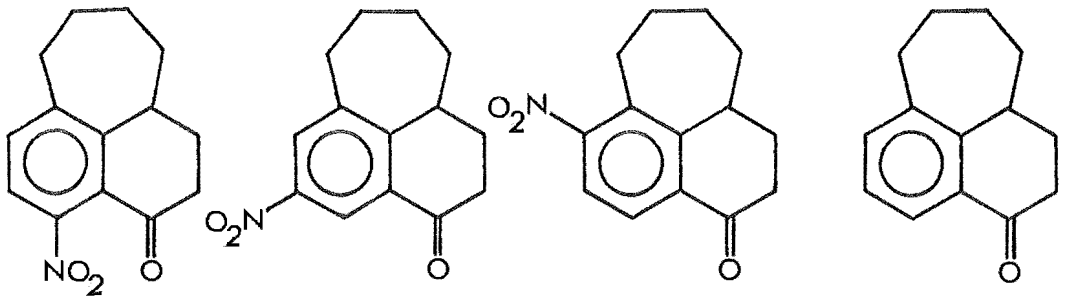

CALCULATED SPECTRUM OF DIENE 68
J_{45} = 4.27
J_{46} = −0.22
J_{56} = 9.63
380 Hz
375
360

FIGURE 13

The three isomeric nitrooxocycloheptanaphthalenes **70-72** were produced concurrently with the dienes **68** and **69**. These were characterised by their infrared, ultraviolet, and n.m.r. spectra data (table VII). The coupling constants for the aromatic protons distinguished the 5-isomer (**71**) from the 4- and 6-isomers (**70** and **72**). The compound **71** has two protons which couple each other at a value within the range expected for a *meta* relationship (0.8-3.0 Hz)[124], whereas **70** and **72** have coupling values which indicate an *ortho* relationship (6.5-9.4 Hz). Compound **71** is further characterised as the 5-isomer by the marked deshielding of its aromatic protons (H^6 by the nitro group and H^4 by both nitro and carbonyl functions) and by the bathochromic displacement of its K-band. The K-band is indicative of the extent of conjugation in the molecule. In the 4- and 6-nitro isomers the carbonyl and nitro functions are substituted *ortho* and *para* to each other such that their mesomeric effects are in direct opposition. Hence the K-bands for these two isomers are only slightly displaced from that found in the parent ketone **14** , and the extinction coefficients of the K-band are decreased. The 5-isomer has a *meta* relationship for these functions and the mesomeric effects of the nitro and carbonyl groups operate independently, with a consequential increase in conjugation. The compounds **70** and **72** were

TABLE VII

Characteristics of the isomeric nitro-3-oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalenes



	70	**71**	**72**	**14**
% of product	26%	34%	1%	-
M.p.	124.5-5.1°	149.5-9.8°	68.0-69.8°	59-60°
I.r.				
ν_{CO}	1705 cm^{-1}	1695	1695	1685
ν_{NO_2}	1535	1520	1530	-
U.v. (n.m., m^2 mol^{-1})				
E	215(1900)	202(1640)	213(1870)	216(1410)
		242(2980)		
K	254(650)	274(1180)	252.5(930)	253.5(1000)
B	304(250)	320(360)	307(240)	300.5(200)
N.m.r. (τ)				
H^4	-	1.42	2.0	2.52
H^5	2.62	-	2.57	2.89
H^6	2.86	1.93	-	2.89
$J_{C_6H_2}$	8 Hz	2.5 Hz	8.5 Hz	

distinguished from each other by the relative chemical shifts of their aromatic protons and their differences in carbonyl and carbon-nitro stretching frequencies. Compound **70** was assigned as the 4-nitro isomer, as its H^6 chemical shift was virtually unaffected (relative to the parent compound **14**) by substitution but its H^5 was deshielded by the adjacent nitro substituent. Furthermore, its $\nu_{C=O}$ and ν_{NO_2} increased. This is the result of steric interaction between the two functions owing to their 1,3 planar relationship and their *ortho* substitution relationship. The former forces the two functions out-of-plane and the latter gives rise to competition for mesomeric withdrawal of charge from the benzene nucleus, both of which cause a decrease in conjugation between the respective functions and the nucleus, and a consequential increase in double bond character of the C-O and N-O bonds. The compound **72** was assigned to the 6-nitro isomer. Both aromatic protons are deshielded relative to the parent ketone, H^4 undergoing the lesser downfield shift, as would be expected. The stretching frequencies of the C=O and NO_2 groups are higher than those observed for monosubstituted keto and nitro benzenes, this being the result of their *para* relationship.

The ratio of the 4-nitro isomer to the 6-nitro isomer isolated was 22:1. This is well in excess of the 7:1 ratio which was calculated using an *o:p* value for the

carbonyl substituent which suggested that for itself an "*ortho* effect" was operative. This is similar to the results obtained for the nitration of anisole in acetic anhydride which were invoked as being an indication that protonated acetyl nitrate was the active agent for nitration in this medium (see page 33).

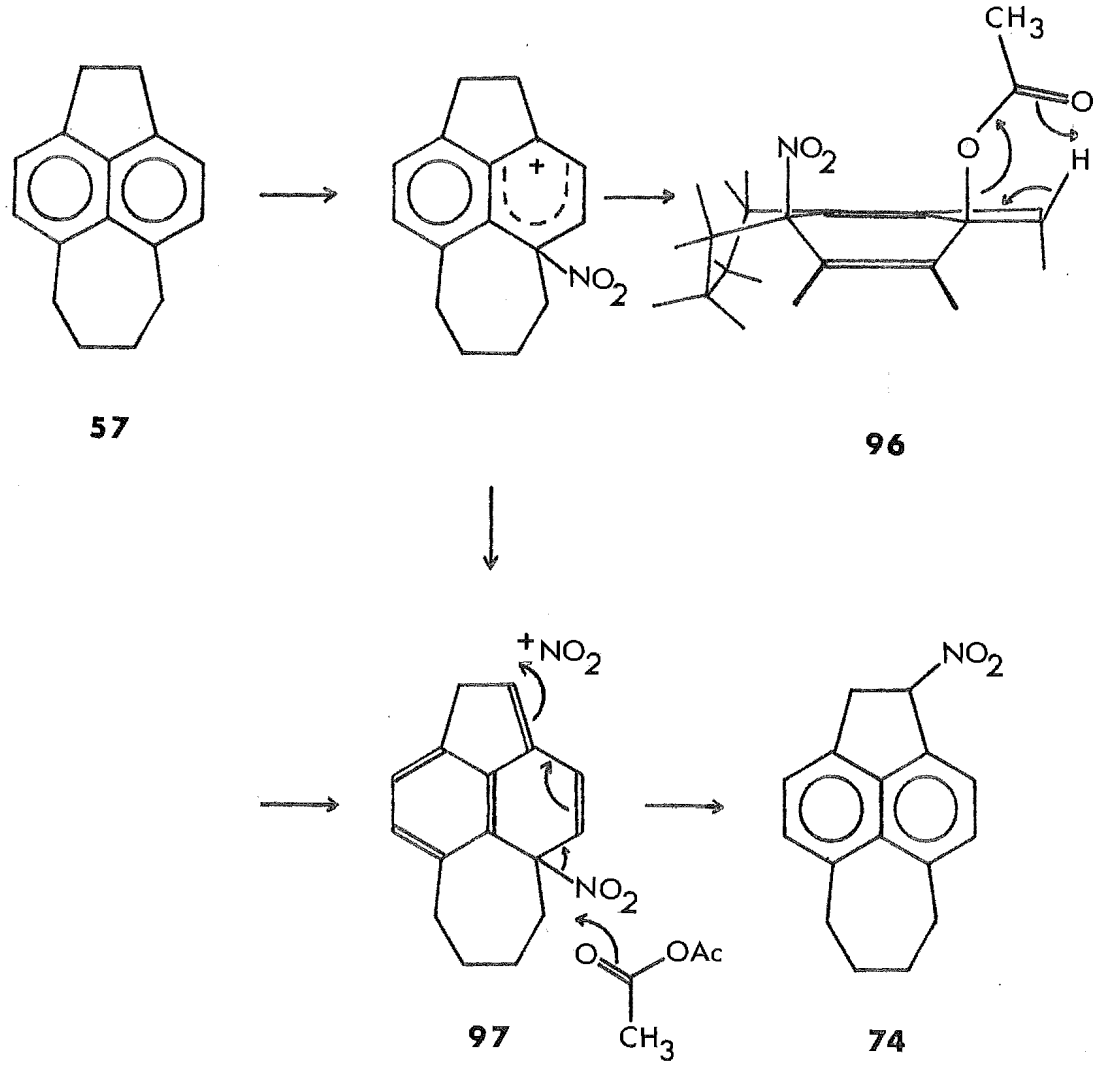
From the nitro-acetoxylation of dipleiadane (**17**) at low temperatures a diene was isolated. At higher temperatures a considerable amount of side-chain nitro compound (homologous to **74**) was obtained, and it appears that as in the case of 1,4-dimethylnaphthalene the diene is intermediate in the formation of the side-chain nitro compound. From the nitro-acetoxylation of acepleiadane (**57**), even when reactions were carried out at low temperatures, it was difficult to isolate a diene, and then only in minor amounts in a largely unreacted product. The main product was invariably the side-chain nitro compound **74**. The diene from acepleiadane is, then, considerably more reactive than that from dipleiadane.

Evidence for the structures of the products was gained by infrared, n.m.r., and mass spectroscopy. The main product from the reaction of acepleiadane was assigned the structure **74**. Its infrared spectrum indicates a compound containing an aliphatic nitro group (ν_{NO_2} = 1555 cm^{-1}), but no acetoxy group. N.m.r. shows that the nitro group is

substituted in the five-membered ring and not the seven-membered ring. The n.m.r. spectrum of the parent hydrocarbon indicates the presence of two distinctly different types of benzylic protons, as it contains a sharp resonance at 6.77 τ (similar to the singlet at 6.68 τ in the spectrum of acenaphthene) and a broader resonance at 6.9 τ (similar to that of dipleiadane at 6.9 τ). In the spectrum of the product the singlet at 6.77 τ is replaced by resonances downfield which have vicinal and geminal coupling constants in agreement with those expected for a CH_2CHNO_2 system.

The diene obtained by low temperature nitroacetoxylation of dipleiadane was assigned the structure on the basis of its infrared and n.m.r. spectra. The quartet centred at 4.165 τ with a coupling constant of 9.5 Hz is similar to that found for the diene of 1,4 dimethyl naphthalene (3.915 τ, 10.3 Hz)[63].

The following mechanism (scheme VIII) is suggested for the formation of the diene and side-chain nitro compound. The hydrocarbon undergoes electrophilic attack at the 4a-carbon as this carbon is activated considerably more by the two-carbon bridge than is the 2a-carbon by the four-carbon bridge[45]. Shortly afterwards the acetoxy group attacks the intermediate Wheland cation at the 2a-position to give the diene **96**. The diene then undergoes intramolecular elimination of acetic acid to form the triene **97**.



SCHEME VIII

The intramolecular elimination is suggested because the increase in strain incurred in the alternative step of going from the Wheland intermediate to the triene would suggest that a driving force for the proton elimination is required. The triene eliminates the nitro group from the 4a-position in order to regain its aromatic resonance stabilisation energy and subsequently adds a second nitro group at the 2-position to form **74**.

Alternatively, formation of the diene from the Wheland intermediate may be reversible, and the Wheland intermediate may lose a proton to form the triene. The reversibility of diene formation is reasonable because the carbon of the C-OAc bond is tertiary. The conversion of one diene to another has been observed for the adducts of 3-bromo-*o*-xylene.

It will be recalled that the diene of acepleiadane appears to be considerably more reactive than the diene from dipleiadane. Models indicate that there is severe 1,4-diaxial ("flagpole") interaction between the acetoxy and nitro groups in the *cis* isomer of the diene of acepleiadane. The *cis* isomer is expected to be the major product, as it is in the case of indan. In the *cis* diene of dipleiadane the severe interaction can be relieved because the more flexible ring system allows the acetoxy and nitro groups to assume quasi equatorial positions.

CONCLUSION

Seven-membered carbocyclic *peri* naphthalenes are best prepared by closing a 1'-butanoate moiety of a 1',2',3',4'-tetrahydronaphthalene into the benzene ring. The closure of a butanoate chain which is substituted in the α position of a fully aromatic naphthalene nucleus results in β- rather than *peri*-closure, unless the *peri* position is highly activated. Alternatively, a seven-membered carbocyclic benzo compound may be prepared on which a propanoate chain may be constructed at the benzylic position which will then close into the benzene ring to form a second six-membered ring. This may then be aromatised to give a cycloheptanaphthalene. On the other hand, six-membered carbocyclic *peri* naphthalenes are best prepared by closing a propanoate attached to the α position of a fully aromatic naphthalene nucleus. When a tetrahydro naphthalene derivative is used the subsequent aromatisation preferentially occurs in the proposed aliphatic pericycle.

The nitro-acetoxylation of indan shows a marked predominance of *cis* adduct formation. This is in contrast to the results obtained for *o*-xylene, and is attributed to the rigid nature of the indan skeleton which facilitates

cis- addition of acetyl nitrate. 3-Oxo-1,2,3,7,8,9,10,10a-octahydrocyclohepta[*de*]naphthalene (**14**) readily undergoes nitro-acetoxy adduct formation, despite its being deactivated towards electrophilic attack. Both its *cis* and *trans* isomers are stable, and this is attributed to mesomeric stabilisation from the carbonyl function. Both 1,2,3,4,7,8,9,10-octahydrodicyclohepta[*de*,*ij*]naphthalene (**17**) and 5,6,7,8-tetrahydrocyclohepta[*fg*]acenaphthene (**57**) form adducts similar to that formed by 1,4 dimethylnaphthalene, but the adduct of **57** is extremely reactive and undergoes further reaction to form a side-chain nitro compound.

REFERENCES

1. *Handbook of Chemistry and Physics*, The Chemical Rubber Company, 1968.

2. L. F. and M. A. Fieser, *J.A.C.S.* **55**, 3010 (1933).

3. D. W. J. Cruickshank, *Acta Cryst.* **10**, 504 (1957).

4. Z. A. Akopyan, R. L. Avoyan, and Y. T. Struchkov, *J. Struct. Chem.* (U.S.S.R.) **4**, 709 (1963).

5. M. B. Jameson and B. R. Penfold, *J. Chem. Soc.* 528 (1965).

6. A. Fischer, R. E. J. Hutchinson, and R. D. Topsom, *J. Chem. Soc.* 5781 (1965).

7. G. Gafner and F. G. Herbstein, *Acta Cryst.* **15**, 1081 (1962).

8. J. Trotter, *Acta Cryst.* **13**, 95 (1960).

9. H. Beyer, K. Sahl, and J. Zemann, *Naturwissenschaften* **52**, 155 (1965).

10. H. W. W. Ehrlich, *Acta Cryst.* **10**, 699 (1957).

11. P. T. Lansbury, *Acc. Chem. Res.* **2**, 210 (1969).

12. P. T. Lansbury, J. F. Bieron, and M. Klein, *J.A.C.S.* **88**, 1477 (1966).

13. L. D. Hall, private communication.

14. L. D. Hall, J. F. Manville, and N. S. Bhacca, *Can. J. Chem.* **47**, 1 (1969).

15. (a) F. A. L. Anet, M. Ahmad, and L. D. Hall, *Proc. Chem. Soc.* 145 (1964).

    (b) F. A. Bovey, F. P. Hood, E. W. Anderson, and R. L. Kornegay, *Proc. Chem. Soc.* 146 (1964).

16. G. V. D. Tiers, *Proc. Chem. Soc.* 389 (1960).

17. F. A. Bovey, E. W. Anderson, F. P. Hood, and R. L. Kornegay, *J. Chem. Phys.* **40**, 3099 (1964).

18. L. D. Hall and J. F. Manville, *Can J. Chem.* **47**, 19 (1969).

19. (a) S. J. Angyal in *Conformational Analysis*, E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, Eds., J. Wiley & Sons, 1965.

(b) R. U. Lemieux in *Molecular Rearrangements*, Part II, P. de Mayo, Ed., John Wiley & Sons, 1964.

20. W. A. Sheppard and C. M. Sharts, *Organic Fluorine Chemistry*, Benjamin, 1969.

21. S. D. Ross, M. Markarian, and M. Schwarz, *J.A.C.S.* **75**, 4967 (1953).

22. W. T. Moreland, D. P. Cameron, R. G. Berg, and C. E. Maxwell III, *J.A.C.S.* **84**, 2966 (1962).

23. J. J. Delpuech and C. Begium, *Bull. Soc. Chim. Fr.* **3**, 791 (1967).

24. E. A. Dixon, University of Victoria, unpublished work.

25. W. R. Hasek, W. C. Smith, and V. A. Engelhardt, *J.A.C.S.* **82**, 543 (1960).

26. V. Balasubramaniyan, *Chem. Rev.* **66**, 567 (1966).

27. B. D. Pearson, *Tetrahedron Letters* **12**, 32 (1961).

28. W. L. Mosby, *J.A.C.S.* **75**, 3348 (1953).

29. B. J. Abadir, J. W. Cook, and D. T. Gibson, *J. Chem. Soc.* 8 (1953).

30. Clar and Marschalk, *Bull. Soc. Chim. Fr.* 433 (1950).

31. G. M. Oskengendler and E. P. Gendrikov, *J. Gen. Chem. U.S.S.R.* **29**, 3857 (1959).

32. R. L. Werner, W. Kennard, and D. Rayson, *Aust. J. Chem.* **8**, 346 (1955).

33. R. D. Topsom, J. Vaughan, and G. J. Wright, *Spectrochim. Acta* **19**, 1859 (1963).

34. R. T. Arnold and E. Rondestvedt, *J.A.C.S.* **68**, 2176 (1946).

35. D. C. Garbutt, K. G. Pachler, and J. R. Parrish, *J. Chem. Soc.* 2324 (1965).

36. P. R. Wells, *Aust. J. Chem.* **17**, 967 (1964).

37. G. O. Dudek, *Spectrochim. Acta* **19**, 691 (1963).

38. C. MacLean and E. L. Makor, *Mol. Phys.* 3, 223 (1960).

39. L. F. Fieser and M. A. Peters, *J.A.C.S.* **54**, 4347 (1932).

40. T. Svensson, *C.A.* **66**, 28564 (1967). [*Arkiv. Kemi*, 27-35 (1966) Eng. Ed.]

41. M. F. Ansell and D. H. Hey, *J. Chem. Soc.* 2874 (1950).

42. A. R. Kon and H. R. Soper, *J. Chem. Soc.* 790 (1939).

43. L. F. Fieser and M. D. Gales, Jr., *J.A.C.S.* **62**, 2335 (1940).

44. W. J. Horton and F. E. Walker, *J.A.C.S.* **74**, 758 (1952).

45. E. Berliner, D. M. Falcione, and J. L. Riemenschneider, *J. Org. Chem.* **30**, 1812 (1965).

46. R. C. Gilmore, Jr., and W. J. Horton, *J.A.C.S.* **73**, 1411 (1951).

47. A. L. Green and D. H. Hey, *J. Chem. Soc.* 4306 (1954).

48. A. J. M. Wenham and J. S. Whitehurst, *J. Chem. Soc.* 3857 (1956).

49. (a) R. D. Topsom and I. K. Lewis, *Aust. J. Chem.* **18**, 923 (1965).

(b) I. K. Lewis, Ph.D. Thesis, University of Canterbury, 1965.

50. A. Fischer, J. Packer, J. Vaughan, and G. J. Wright, *Proc. Chem. Soc.* (1961) 369; *J. Chem. Soc.* 3687 (1964).

51. P. G. E. Alcorn and P. R. Wells, *Aust. J. Chem.* **18**, 1377 (1965).

52. A. Fischer, A. J. Read, and J. Vaughan, *J. Chem. Soc.* 3691 (1964).

53. P. B. D. De la Mare and J. H. Ridd, *Aromatic Substitution*, Butterworths, 1959, p. 84.

54. R. O. C. Norman and G. K. Radda, *J. Chem. Soc.* 3030 (1961).

55. K. Halvarson and L. Melander, *Arkiv. Chemi.* 11, 77 (1957).

56. G. J. Wright, Ph.D. Thesis, University of Canterbury, 1965.

57. R. B. Taylor, *J. Chem. Soc.* (B) 727 (1966).

58. D. J. Blackstock, Ph.D. Thesis, University of Canterbury, 1970.

59. (a) J. H. Ridd, *Studies on Chemical Structure and Reactivity*, Methuen, 1966, p. 133.

(b) P. B. D. De la Mare and R. Koenigsburger, *J. Chem. Soc.* 5327 (1964).

60. (a) D. J. Blackstock, A. Fischer, K. E. Richards, J. Vaughan, and G. J. Wright, *Chem. Comm.* 641 (1970).

(b) D. J. Blackstock, J. R. Cretney, A. Fischer, M. P. Hartshorn, K. E. Richards, J. Vaughan, and G. J. Wright, *Tetrahedron Letters* 32, 2793 (1970).

(c) D. J. Blackstock, Ph.D. Thesis, University of Canterbury, 1970.

61. (a) P. B. D. De la Mare, M. D. Johnson, J. S. Lomas, and V. Sanchez del Olmo, *J. Chem. Soc.* (B) 827 (1966).

(b) G. Cum, P. B. D. De la Mare, J. S. Lomas, and M. D. Johnson, *J. Chem. Soc.* (B) 244 (1967).

62. R. Robinson, *J. Chem. Soc.* (B) 1289 (1970).

63. A. Fischer and A. L. Wilkinson, *Chem. Comm.* (1971).

64. M. F. Ansell and S. S. Brown, *J. Chem. Soc.* 3956 (1958).

65. W. Dieckmann, *Ber.* 32, 2227 (1899).

66. A. G. Anderson and S. Y. Wang, *J. Org. Chem.* 19, 280 (1954).

67. R. C. Gilmore, *J.A.C.S.* **73**, 5879 (1951).

68. A. C. Cope and L. Field, *J.A.C.S.* 71, 1591 (1949).

69. J. W. Cook, R. Philip, and A. R. Somerville, *J. Chem. Soc.* 169 (1948).

70. W. S. Johnson, H. C. E. Johnson, and J. W. Peterson, *J.A.C.S.* **67**, 1360 (1945).

71. *Organic Reactions*, Vol. 14, p.p. 435 and 446, 1965.

72. W. S. Johnson and W. E. Heinz, *J.A.C.S.* 71, 2917 (1949).

73. D. C. Ayres, *Carbanions in Synthesis*, Oldbourne Press, 1966.

74. W. R. Vaughan, S. C. Bernstein, and M. E. Lorber, *J. Org. Chem.* **30**, 1790 (1965).

75. M. S. Newman, *J.A.C.S.* **60**, 2949 (1938).

76. M. S. Newman and T. J. O'Leary, *J.A.C.S.* 68, 258 (1946).

77. P. H. Gore, *Chem. Rev.* **55**, 238 (1955).

78. D. J. Cram, M. R. V. Sahyun, and G. R. Knox, *J.A.C.S.* **84**, 1734 (1962).

79. D. J. Cram and R. C. Helgeson, *J.A.C.S.* **88**, 3515 (1966).

80. L. F. Fieser, *J.A.C.S.* **54**, 4963 (1932).

81. M. E. C. Biffin, L. Crombie, and J. A. Elvidge, *J. Chem. Soc.* 7500 (1965).

82. H. O. House, E. J. Grubbs, and W. F. Gannon, *J.A.C.S.* **82**, 4099 (1960).

83. L. V. Johnson, F. Smith, M. Stacey, and J. C. Tatlow, *J. Chem. Soc.* 4710 (1952).

84. S. D. Ross, M. Finkelstein, and R. C. Petersen, *J.A.C.S.* **80**, 4327 (1958).

85. W. C. Smith, *Angew. Chemie* Int. Ed. **1**, 467 (1962).

86. J. T. Gerig and J. D. Roberts, *J.A.C.S.* 88, 2791 (1966).

87. S. L. Spassov, D. I. Griffith, E. S. Glazer, K. Nagarajan, and J. D. Roberts, *J.A.C.S.* **89**, 88 (1967).

88. G. A. Boswell, *J. Org. Chem.* **31**, 991 (1966).

89. F. G. Bordwell and E. W. Garbisch, *J.A.C.S.* **82**, 3588 (1960).

90. Technique developed by Dr. A. L. Wilkinson.

91. A. L. Wilkinson, private communication.

92. M. S. Newman and H. V. Zahn, *J.A.C.S.* 65, 1099 (1933).

93. T. A. Geissman and L. Morris, *J.A.C.S.* 66, 716 (1944).

94. R. D. Haworth, *J. Chem. Soc.* 1125 (1932).

95. L. F. Somerville and C. F. H. Allen, *Org. Syn. Coll.* Vol. II, 82 note 9.

96. W. S. Johnson, A. R. Jones, and W. P. Schneider, *J.A.C.S.* **72**, 2395 (1950).

97. J. T. Plati, W. H. Strain, and S. L. Warren, *J.A.C.S.* 65, 1274 (1943).

98. A. Ali, R. D. Desai, R. F. Hunter, and S. M. Makhdhum Muhammad, *J. Chem. Soc.* 1015 (1937).

99. H. Adkins and H. R. Billica, *J.A.C.S.* **70**, 697 (1948).

100. T. A. Crabb and K. Schofield, *J. Chem. Soc.* 4276 (1958).

101. B. Riegel and J. G. Burr, *J.A.C.S.* **70**, 1070 (1948).

102. G. Schroeter, *Ber.* **57**, 2025 (1924).

103. G. Schroeter, *Ber.* **63**, 1308 (1930).

104. K. Ziegler, *Ann.* **551**, 118 (1942).

105. R. B. Hasbrouck and M. A. Speilman, *C. A.* **50**, 10804i (1956).

106. M. F. Grundon, H. B. Henbest, and M. D. Scott, *J. Chem. Soc.* 1855 (1963).

107. J. A. Moore and D. E. Reed, *Org. Syn.* 41, 16 (1961).

108. G. Sweifel and H. C. Brown, *Org. Reactions* 13, 28 (1963).

109. W. S. Johnson, M. Neeman, S. P. Birkeland, and N. A. Fedoruk, *J.A.C.S.* 84, 991 (1962).

110. *Elsevier's Encyclopaedia of Organic Chemistry*, Elsevier, 1948.

111. Scholl and Tritsch, *Monatsh.* 32, 997 (1911).

112. L. F. Fieser and M. A. Peters, *J.A.C.S.* 54, 3744 (1932).

113. E. A. Braude and E. R. H. Jones, *J. Chem. Soc.* 498 (1945).

114. H. Budzikiewicz, C. Djerassi, and D. H. Williams, *Mass Spectrometry of Organic Compounds*, Holder-Day, 1967.

115. R. P. Linstead and H. N. Rydon, *J. Chem. Soc.* 580 (1933).

116. L. Doub and J. M. Vanderbelt, *J.A.C.S.* 71, 2414 (1949).

117. J. D. Roberts and C. Green, *J.A.C.S.* 68, 214 (1946).

118. R. B. Clayton, A. Crawshaw, H. B. Henbest, E. R. H. Jones, B. J. Lovell, and G. W. Wood, *J. Chem. Soc.* 2009 (1953).

119. R. A. Friedel and M. Orchin, *Ultraviolet Spectra of Aromatic Compounds*, John Wiley & Sons, 1951.

120. W. Herz and J. L. Rogers, *J.A.C.S.* 75, 4499 (1953).

121. A. L. Wilds, L. W. Beck, W. J. Close, C. Djerassi, J. A. Johnson, T. L. Johnson, and C. H. Skunk, *J.A.C.S.* 69, 1985 (1947).

122. G. S. Hammond in *Steric Effects in Organic Chemistry*, M. S. Newman, Ed., John Wiley & Sons, 1956.

123. A. E. Gillam and E. S. Stern, *An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry*, Edward Arnold, 1958.

124. F. A. Bovey, *Nuclear Magnetic Resonance Spectroscopy*, Academic Press, 1969.

125. D. H. Wiffen and H. W. Thompson, *J. Chem. Soc.* 268 (1945).

126. M. P. Groenewege, *Spectrochim. Acta* **11**, 579 (1957).

127. H. H. Jaffé and M. Orchin, *Theory and Applications of Ultraviolet Spectroscopy*, John Wiley & Sons, 1962.

128. S. J. Cristol, W. Barasch, and C. H. Tieman, *J.A.C.S.* **77**, 583 (1955).

129. E. W. Garbisch and M. G. Griffith, *J.A.C.S.* **90**, 3590 (1968).

130. L. F. Fieser and W. C. Lothrup, *J.A.C.S.* **58**, 2050 (1936).

131. R. M. Silverstein and G. C. Bassler, *Spectrometric Identification of Organic Compounds*, John Wiley & Sons, 1968.

132. J. D. Swalen and C. A. Reilly, *J. Chem. Phys.* **37**, 21 (1962).

133. J. D. Swalen in *Computer Programs for Chemistry*, D. F. de Tar, Ed., Vol. I, W. A. Benjamin, 1968.

134. R. F. C. Claridge and B. M. Peake, *Molecular Physics* **19**, 737 (1970).

ACKNOWLEDGMENTS

Financial support from the New Zealand University Grants Committee, the University of Victoria, British Columbia, and the National Research Council of Canada is gratefully acknowledged.

Professor A. Fischer is thanked for his generous giving of time in the direction of the major part of this research.